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AN EXPERIMENT UPON THE INFLUENCE OF THE FINENESS OF GRINDING UPON THE CLINKERING OF PORTLAND CEMENT.

BY E. D. CAMPBELL AND S. BALL.

Received September 11, 1903.

IN A paper entitled "Some Preliminary Experiments upon the Clinkering of Portland Cement,"[1] one of the authors has reported some results obtained in a laboratory rotary cement kiln. The calcium carbonate used in all the preliminary experiments was in the form of a very light marl, so that when clinkering took place it was accompanied by very marked contraction in volume. It was suggested that a burning on raw material, such as is used in the cement mills of Eastern Pennsylvania, might give somewhat different results from those obtained from the light marl mixed with clay, and so it was decided to make a couple of experiments with rock-cement mixtures. The material employed in the two experiments, to be later described, was a ground raw mixture just as it is fed into the rotary for the dry process. This raw mixture is that used by one of the best Lehigh Valley mills and was furnished for these experiments through the courtesy of the management.

[1] This Journal, **24**, 969.

Before detailing the experiments made upon the cement-rock mixture, we wish to describe the method now employed in this laboratory for determining the actual temperature attained by the pieces of clinker in passing through the rotary. In the first papers publisher by one of us on "A Rotary Cement Kiln for use in the Laboratory,"[1] the method of measuring the temperature of the furnace is described. In this method, the temperature attained by a Le Chatelier thermocouple, insulated with porcelain tubing and protected with sheet platinum, is observed. But this temperature was supposed to be 35° to 40° C. lower than that attained by the clinker. The temperatures given in the paper, first quoted in this article as representing the temperatures attained by the clinker, are based on the assumption that the clinker becomes 35° hotter than the protected thermocouple. It is true that if the bare couple be placed in the rotary, it will reach a higher temperature than that shown by the protected couple. This does not, however, warrant the assumption that pieces of clinker in contact with the rotary lining will attain as high a temperature as the bare couple. It was because of the feeling that the relation between the temperature of the clinker and that of the fixed couple was not what we have assumed in our previous work, that a series of experiments was made to determine the relation of these temperatures. A calibration of the fixed thermocouple was made, as in our previous work, by careful comparison of the electromotive force with that of a couple standardized by the physikalische-technische Reichsanstalt. The electromotive force at the melting-point of strictly pure platinum was also determined, and used in the calibration. Although an entirely new set of thermocouples and galvanometer were used in the present experiments, the temperatures recorded for the fixed thermocouple agreed within the limits of experimental error with those of our previous work. In order to determine the relation between the temperature attained by pieces of clinker and that observed at the fixed thermocouple, the following method was used: About 2 kg. of magnesite brick were crushed, and, after mixing with one-ninth its weight of a rather fusible clay, was ground to a fine powder. This mixture was moistened with enough water to enable it to be rolled out and cut into cubes, of about three-eights inch, which were then dried. These cubes were passed through

[1] This Journal, **24**, 248.

the rotary at a full heat, the result being hard, well-sintered, but infusible "magnesite clinkers." A Seger cone of the standard size was placed in an assay muffle, the temperature of which was then raised until the top of the cone bent over enough to touch the bottom—the method usually employed for standardizing these cones. The extent to which this cone had rounded at the corners, etc., gave a standard with which to compare pieces of cone which had passed through the rotary. In testing the temperatures attained by the clinker in the rotary, a cone of low fusing-point (990° C.) was first employed. Cones of this softening-point were broken into pieces of as nearly as possible the same size as the "magnesite clinker." When the rotary was filled with the magnesite, a piece of the cone was fed with the magnesite every four or five minutes. The temperature was gradually raised until the pieces coming out showed an extent of softening or fritting equal to that of the standard cone. This point was usually quite sharply defined, as when the pieces of cone attained this condition they would begin to stick either to each other or to adjacent pieces of magnesite. In this way our experiments were made with a number of cones of a higher softening-point, up to between 1500° and 1600° C. These experiments showed that at the lower temperature the clinker does not get as hot as the fixed couple, but that it approaches the temperature of the fixed couple as the heat is raised, until at about 1270° C. they are equal. At temperatures above 1270° C., the clinker is hotter than the thermocouple, this difference amounting to very nearly 19° at 1600° C. The relation of the "clinker temperature" to that observed at the fixed couple is shown in the following table:

TABLE I.

Observed temperature. °C.	Clinker temperature. °C.	Difference.
1000	984	—16
1100	1090	—10
1200	1196	— 4
1300	1302	+ 2
1400	1407	+ 7
1500	1513	+13
1600	1619	+19

The "clinker temperatures," reported in experiments 104-105 to be described, were determined according to this table. The "clinker temperature," in our previously reported work, can be

easily derived by first subtracting 35°, thus obtaining the "observed temperature," and then applying the necessary correction according to the above table.

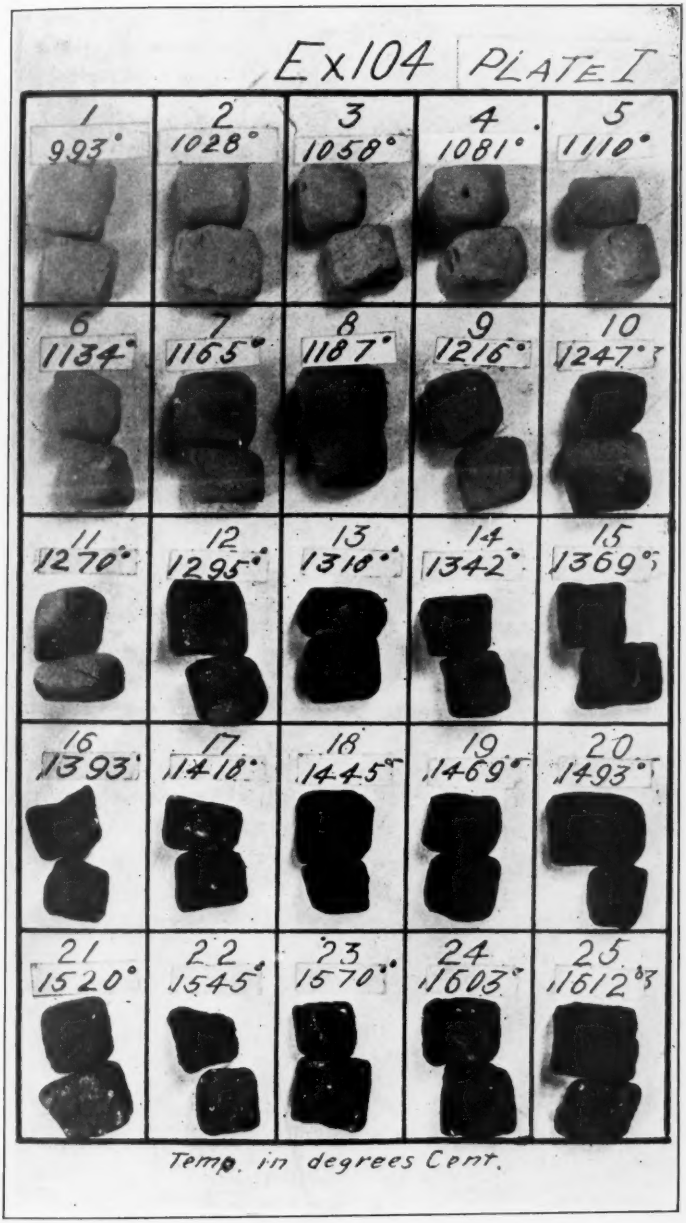
EXPERIMENT 104.

The material used in this experiment was, as mentioned earlier in this paper, the ground raw mixture just as it is fed into the rotaries of one of the leading Eastern cement-mills employing the dry process. The chemical composition of this mixture will be described under Experiment 105. A mechanical analysis of the raw mixture gave the following figures:

	Per cent.
Retained on 50-mesh sieve	3.1
" " 100 " "	11.3
" " 200 " "	13.2
Through 200-mesh sieve	72.4

This raw mixture was moistened with just enough water to allow it to be rolled out and cut into small cubes, as done in our previous work. The rotary furnace was fed with this prepared material, and samples of from 80 to 100 grams each were collected at twenty-five different temperatures ranging from 993° to 1612° C. When the desired amount of clinker had been collected at any given temperature, the temperature of the furnace was raised up to the next higher point desired, and the first 60 to 70 grams of clinker leaving the furnace rejected before the final sample was kept. The 60 to 70 grams of clinker, rejected between the sample saved, is the amount required to fill the furnace from the hot zone to the discharge end and, consequently, represents the clinker formed at heats intermediate between the desired temperatures. The change in appearance of the samples of clinker is shown in Plate I, made from a full-sized photograph.

Samples of these clinkers were ground with 1.5 per cent. calcium sulphate (dehydrated gypsum). The methods employed for determining the water required for normal consistency, the initial and final sets, and boiling tests were those employed in our previous experiments. The data obtained from Experiment 104 are summarized in the following table:


Ex104 PLATE I
1 993°
2 1028°
3 1058°
4 1081°
5 1110°
6 1134°
7 1165°
8 1187°
9 1216°
10 1247°
11 1270°
12 1295°
13 1318°
14 1342°
15 1369°
16 1393°
17 1418°
18 1445°
19 1469°
20 1493°
21 1520°
22 1545°
23 1570°
24 1603°
25 1612°
Temp. in degrees Cent.

25	1612	23½	..	17	3	48	Very slightly warped, cracked, very strong.

TABLE II, EXPERIMENT 104.

Sample number.	Clinker temperature.	Water. Per cent.	Initial set. Hours.	Initial set. Minutes.	Final set. Hours.	Final set. Minutes.	Boiling test.
1	993	39	..	24	3	53	Perfect pat.
2	1028	48	..	30	3	58	" "
3	1058	54	..	30	4	20	" "
4	1081	66	..	35	4	33	" "
5	1110	76	..	41	5	38	Badly cracked.
6	1134	75	..	48	6	5	Badly cracked, broken up, loose from glass.
7	1165	76	..	17	1	45	Cracked after twenty-four hours. Boiling test, badly cracked and broken up.
8	1187	60	..	1	..	16	Slightly cracked and warped, loose from glass, quite strong.
9	1216	55	..	½	..	19	Loose from glass, moderately strong.
10	1247	47	..	1	..	6	Badly cracked, disintegrated, very weak.
11	1270	43	..	1	..	4	Warped, cracked, almost completely disintegrated.
12	1295	38	..	2	..	4½	" " " " "
13	1318	37	..	3	..	11	Completely disintegrated.
14	1342	32	..	7	1	38	" "
15	1369	31½	..	12	1	26	" "
16	1393	30½	..	23	4	8	Completely disintegrated, coarse-grained.
17	1418	28½	..	33	4	..	Almost completely disintegrated.
18	1445	26	..	21	3	48	" " "
19	1469	26	..	33	3	50	Slightly warped, badly cracked, very weak.
20	1493	26½	..	13	2	53	Slightly warped, cracked, very weak.
21	1520	25½	..	34	4	9	Badly warped, cracked, very weak.
22	1545	25	1	..	5	..	Slightly warped, cracked, quite strong.
23	1570	24	..	50	4	6	" " " " "
24	1603	23	..	32	3	50	Badly warped, cracked very weak. (This sample was ground too coarsely.)
25	1612	23½	..	17	3	48	Very slightly warped, cracked, very strong.

The appearance of the pats from Experiment 104 is shown in Plates II, III, IV and V.

EXPERIMENT 105.

The material used in this experiment was the same raw material as that used in Experiment 104. Before adding water and molding into cubes for burning, the dry mixture was ground in a pebble mill for five hours. The jar in which the grinding was done had a special lining made for this purpose of the best Berlin porcelain. The pebbles used were carefully selected, smooth flints. A mechanical analysis of the mixture after five hours' grinding gave the following results:

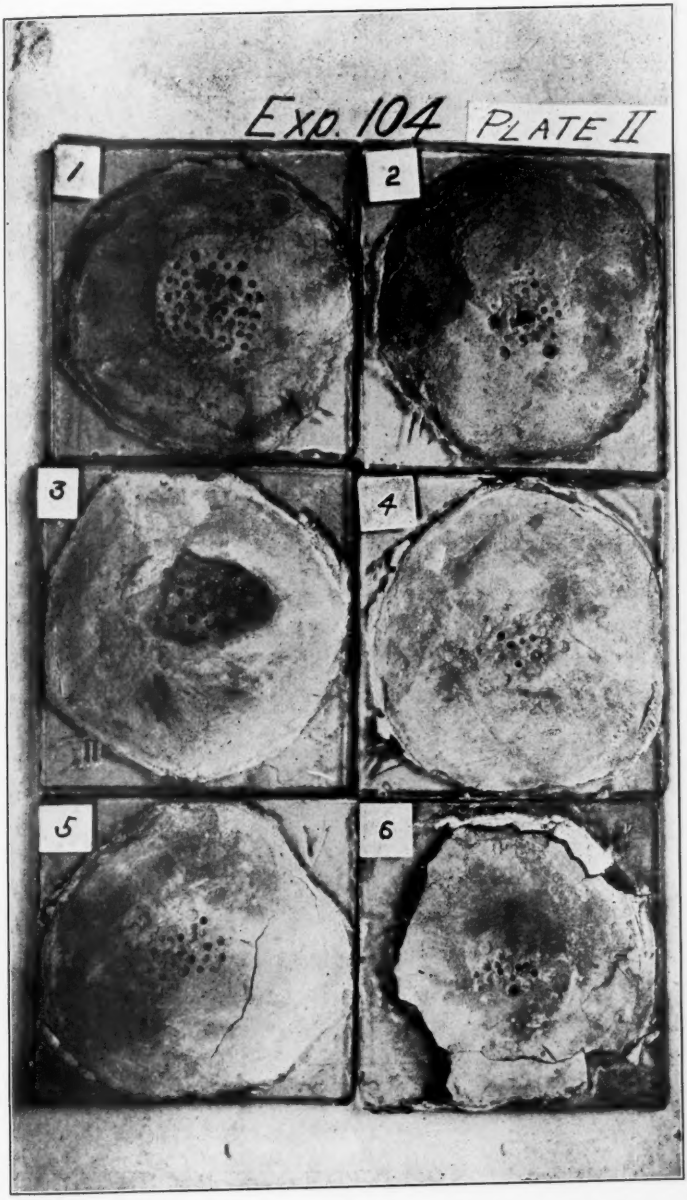
	Per cent.
Retained on 100-mesh sieve	0
" " 200 " "	2
Through 200-mesh sieve	98

That material ground in this porcelain-lined jar mill does not take up sufficient impurities to seriously alter the composition was determined in two ways: First, 2 kilograms of crushed crystalline calcite were ground for three hours. The combined per cent. of silica, alumina, and ferric oxide before grinding was 0.71; after grinding three hours, the material showed 0.75 per cent. Second, the clinker from Experiment 104 gave total silica and undecomposed silicates, 22.02 per cent., while that from Experiment 105 gave 22.06 per cent.

The raw mixture used had the following composition: SiO_2, 14.09; Al_2O_3, 5.94; Fe_2O_3, 1.67; CaO, 41.21; MgO, 1.76; SO_3, 0.39; loss on ignition, 34.60. The finely ground, raw material was mixed as in the previous experiment with enough water to allow it to be rolled out and cut into cubes for burning. From this prepared material, twenty-four samples of the clinker were collected at temperatures ranging from 1022° to 1627° C.

The composition of the clinker produced at some of the higher temperatures was as follows: Total SiO_2, 21.55; total Al_2O_3, 9.09; Fe_2O_3, 2.56; CaO, 63.01; MgO, 2.73; SO_3, 0.60; total 99.56 per cent.

The molecular ratios in the clinker calculated to the basis of 100 molecules of silica are as follows: SiO_2, 100; Al_2O_3, 24.9; Fe_2O_3, 4.5; CaO, 315.2; MgO, 19.1. The appearance of the clinkers is shown in Plate VI.


EXP. 104
PLATE II
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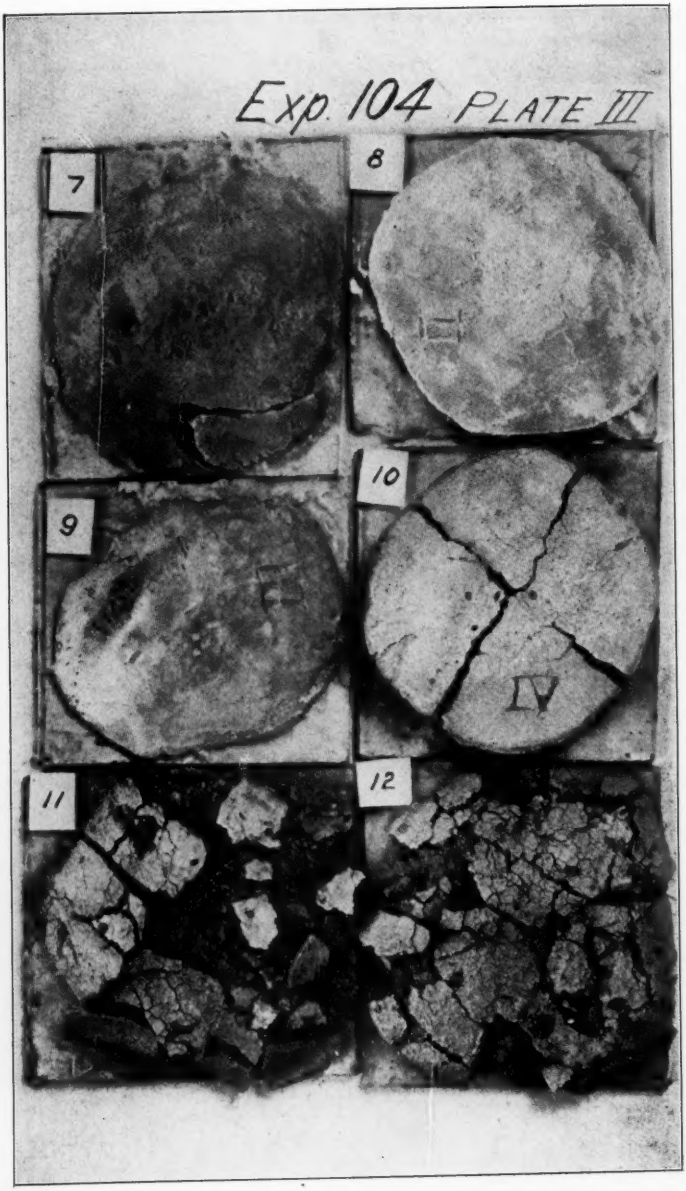
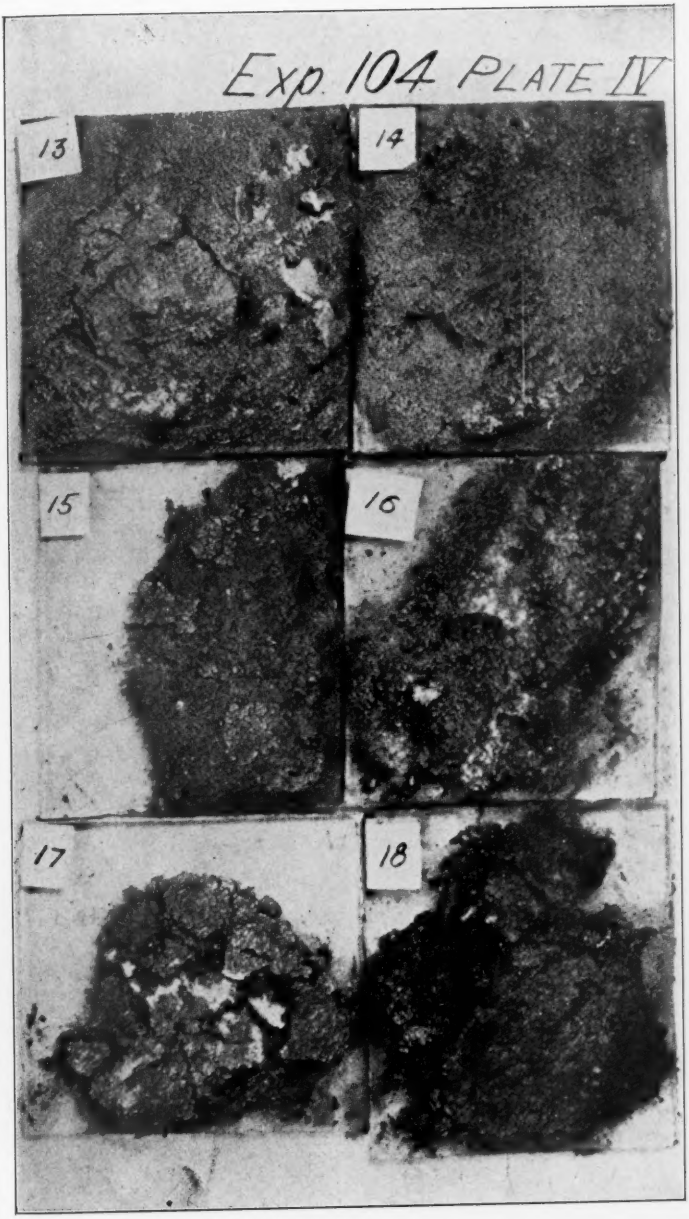
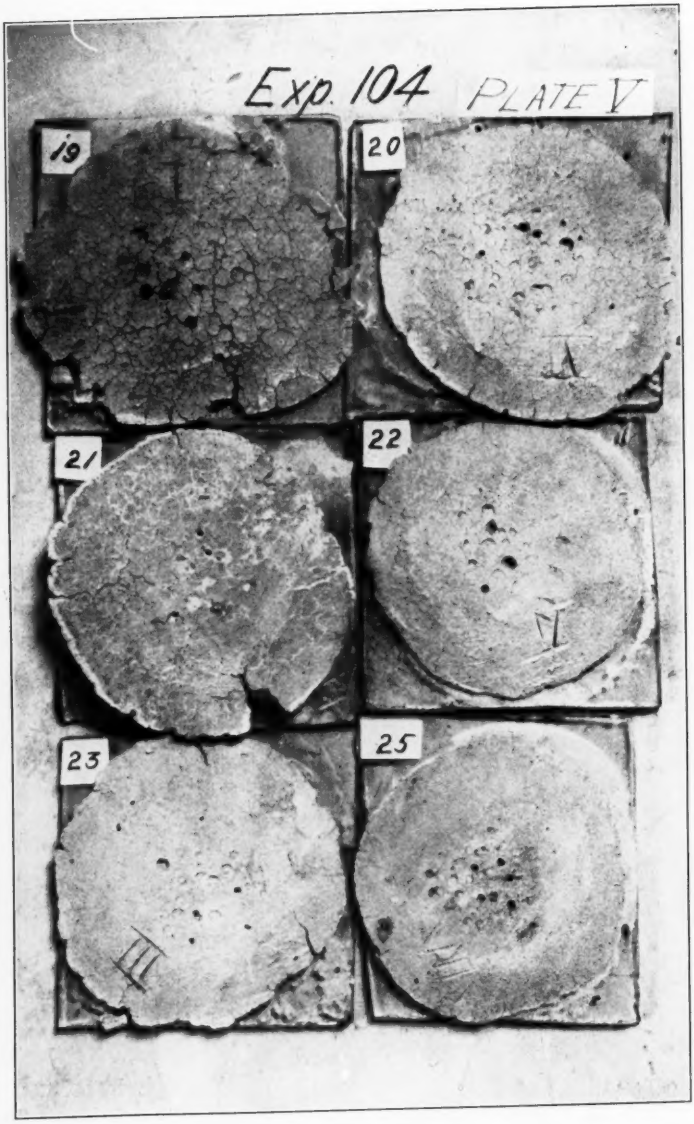
Exp. 104 PLATE III

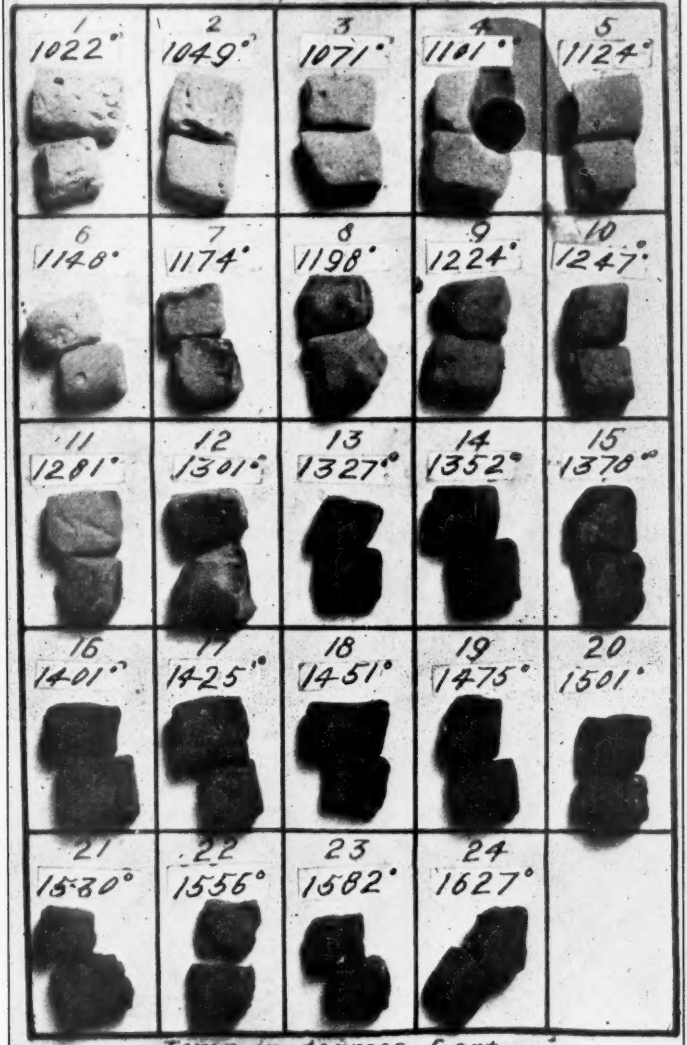


Exp. 104 PLATE IV




Exp. 104
PLATE V
19
20
21
22
23
25

Exp. 105 PLATE VI



Temp. in degrees Cent.

TABLE III, EXPERIMENT 105.

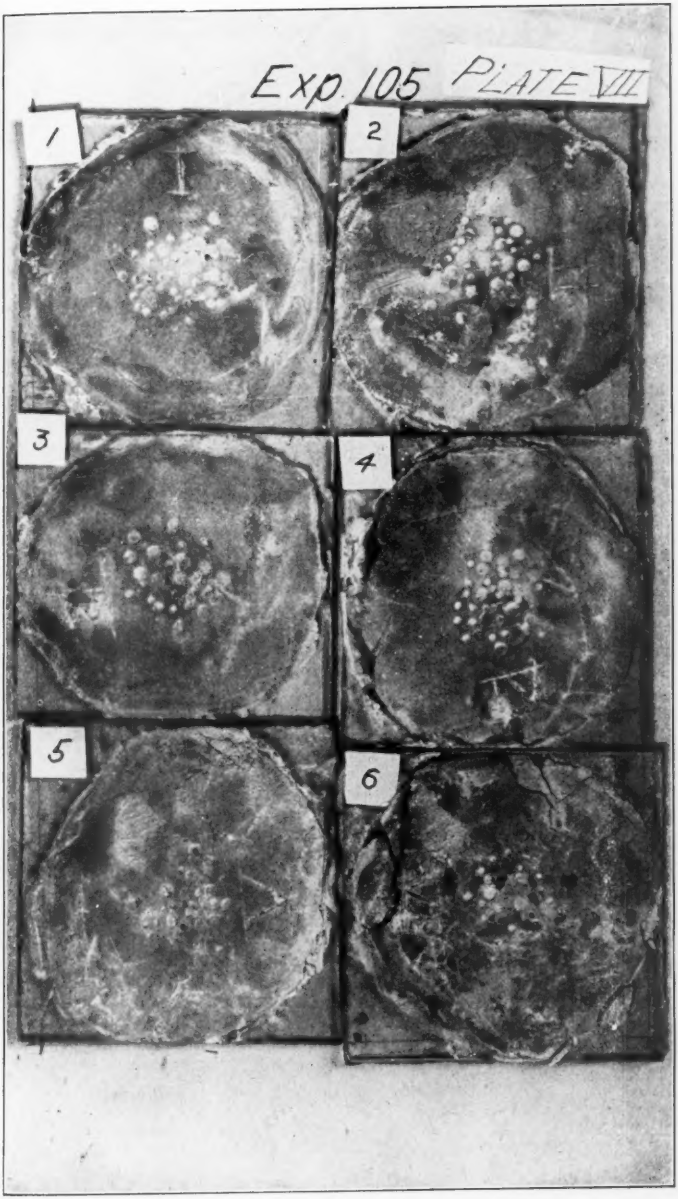
Sample number.	Clinker temperature.	Water. Per cent.	Initial set. Hours.	Initial set. Minutes.	Final set. Hours.	Final set. Minutes.	Boiling test.
1	1022	49	..	11	5	10	Perfect pat, quite strong.
2	1049	53	..	18	7	..	" " " "
3	1071	61	..	23	7	20	" " " "
4	1101	73	..	39	7	47	Loose from glass, slightly cracked, quite strong.
5	1124	77	..	27	7	25	Slightly warped, cracked, quite weak.
6	1148	78	..	7	5	13	Badly warped, cracked, very weak.
7	1174	77	..	5	4	..	Badly cracked, very weak.
8	1198	69	..	½	..	16	Badly cracked, warped, very weak.
9	1224	64	..	½	..	4	" " " " "
10	1247	62	..	½	3	40	" " " " "
11	1281	54	..	1	5	..	Badly warped and disintegrated.
12	1301	46	..	1	..	46	Very badly warped and disintegrated.
13	1327	44	..	1	..	29	Very badly warped, cracked, almost completely disintegrated.
14	1352	40	..	3	..	21	Completely disintegrated.
15	1378	37	..	3½	..	27	" "
16	1401	33½	..	18	3	15	" "
17	1425	32	..	10	2	22	Badly warped and cracked, almost completely disintegrated.
18	1451	30	..	14	4	45	Slightly warped, cracked, loose from glass, but quite strong.
19	1475	28	1	5	4	40	Perfect pat.
20	1501	27	..	32	4	22	" "
21	1530	28½	..	1	3	53	Perfect pat, sample slightly off color.
22	1556	26½	..	32	4	..	Perfect pat.
23	1582	24	..	21	4	..	" "
24	1627	24½	..	10	3	50	" "

Samples of these clinkers were ground with 1.5 per cent. calcium sulphate (dehydrated gypsum), and determinations of water required for normal consistency, initial and final sets, and boiling tests were made as in the previous experiment. The data obtained from Experiment 105 are summarized in Table III.

The appearance of the pats from Experiment 105 is shown in Plates VII, VIII, IX and X.

In considering the samples of Experiment 105, the conditions of formation of sample No. 21 should be taken into account. Up to sample No. 20 inclusive, the color of the clinker darkened progressively with increase of temperature. Owing to some difficulty with the hydrocarbon burner, the gasoline jet would not draw in sufficient air for complete combustion above 1501° C., at which temperature No. 20 was burned. When the valve was opened a little wider in order to raise the temperature, a small amount of carbon monoxide was produced in the gas with the result that the clinker became a little lighter rather than darker in color. Oxygen was introduced from the time No. 21 was collected with the result that Nos. 22, 23 and 24 all had the deep blackish brown color characteristic of properly burned clinker. Whether the quick initial set of No. 21 was due to the slight reducing conditions in the furnace at the time of burning, we are not prepared to state positively. It will be noticed that with the exception of No. 21, the time of the initial set, after a perfect hot test was obtained, decreased with increased temperature, but the time between the initial and the final set for these same samples was nearly constant. The influence of the atmosphere within the furnace upon the time of setting as well as upon the other properties of cement, we hope to investigate more closely at a later date.

It was thought that some light might be thrown upon the reactions of clinkering by dissolving, in dilute hydrochloric acid, some of the clinkers produced at temperatures at which there were marked changes in the physical properties of the cement. The first method employed was that usually recommended; that is, three successive boilings for five minutes each with 10 per cent. hydrochloric acid. A number of experiments, however, proved that more complete decomposition could be effected by digestion with hot hydrochloric acid than with successive boilings. If the


Exp. 105 Plate VII
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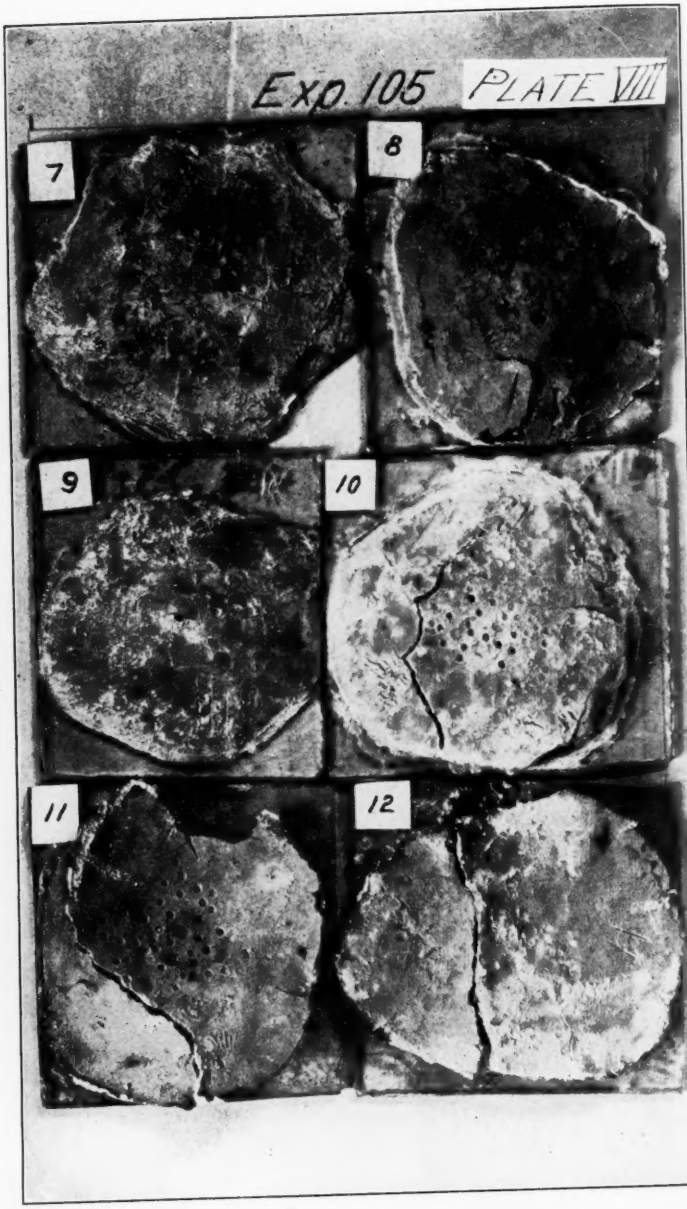
EXO. 105
PLATE VIII
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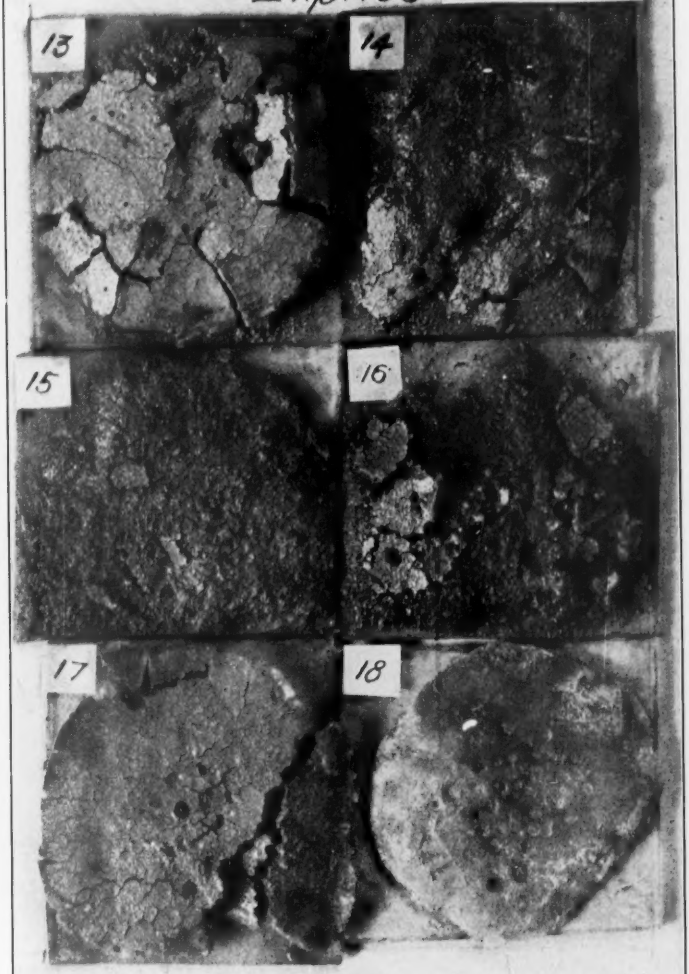
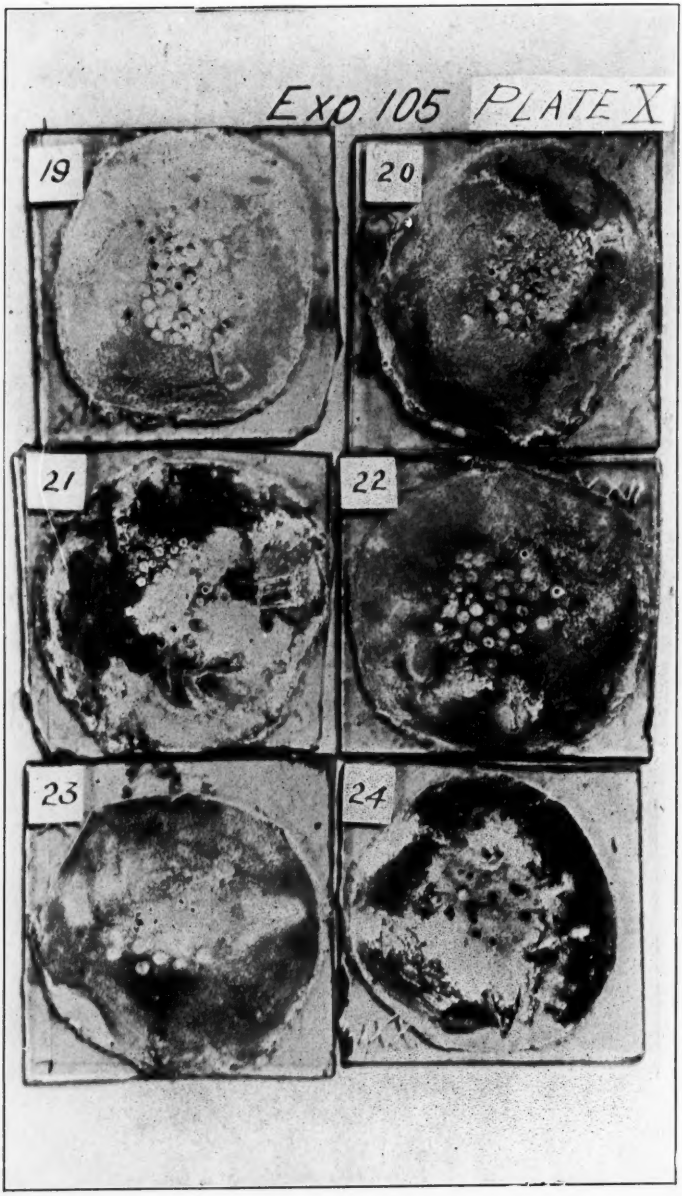
12

EXP. 105 PLATE IX




EXO. 105 PLATE X
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acid solution containing the cement in suspension is boiled, gelatinous silicic acid seems to deposit on some of the larger particles of cement, thus preventing the acid from effecting complete decomposition. It was found that if 0.5 gram of the cement is placed in 50 cc. of water and this boiled for from two to three minutes, then removed from the hot plate and 5 cc. hydrochloric acid (sp. gr. 1.20) added, and the solution stirred for about five minutes without further heating, the silicic acid set free nearly all remains in solution and a more perfect decomposition is apparently effected than by boiling.

Accordingly, six of the samples were treated in this way. The total silica having been determined, samples of the various clinkers examined were first boiled with water, to which was then added the hydrochloric acid, and after a few minutes' stirring the solution was filtered. The residue, after washing with acidified water until free from soluble salts, was gently ignited and weighed. The difference in weight between this residue and that obtained by the usual method of decomposition, evaporation to dryness, etc., for total insoluble residue, was taken as "SiO_2 soluble in HCl." The residue insoluble in hydrochloric acid was boiled in a platinum dish with 10 per cent. sodium carbonate, filtered, washed, and weighed. The loss thus obtained was reported as "SiO_2 soluble in Na_2CO_3." The residue from the digestion with sodium carbonate was treated with hydrofluoric acid, the loss giving the "SiO_2 by HF." The final residue was reported as "Residue from HF." With the exception of No. 1, which gave a loss on ignition of 21.03 per cent., the decomposition of the calcium carbonate of the samples examined was complete. The action of hydrochloric acid, etc., upon the six samples examined is summarized in the following table:

TABLE IV.

Sample number.	Clinker temperature.	SiO_2 sol. in HCl.	SiO_2 sol. in Na_2CO_3.	SiO_2 by HF.	Residue from HF.
1	1022	5.67	1.18	10.67	4.54
6	1148	8.77	0.86	8.34	4.09
9	1224	13.92	1.19	4.09	2.86
14	1352	17.91	3.61	0.28	0.26
19	1475	19.99	1.23	0.42	0.42
24	1625	20.03	1.07	0.50	0.46

Although the results given in Table IV cannot be considered as final and will need confirmation, they indicate one or two rather interesting points.

It will be noticed that the silica, soluble in hydrochloric acid, increases with the increase in the temperature at which the clinker is produced. The silica, soluble in sodium carbonate, however, reaches a maximum in sample No. 14, burned at 1352°. The total insoluble residue after treatment with sodium carbonate, usually reported as "undecomposed silicate," is smallest (0.54 per cent.) in this same sample. The amount of undecomposed silicates seems to increase with rise in temperature above 1352°, and the proportion of silica given off on treating these undecomposed silicates with hydrofluoric acid, is about one-half their weight.

These results would go to indicate that probably all of the original silicates were converted into readily decomposable basic silicates by the time a temperature of 1352° was reached, and that the increased amount of undecomposed silicates found in the high numbers may be due to the more acid silicates left in the magma, from which the tricalcium silicate or other true cement-forming material has separated.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE THEORIES OF INDICATORS.[1]

BY JULIUS STIEGLITZ.

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IN CONNECTION with the use of indicators in the titration of acids and alkalies there are two main questions of theoretical interest: First, what chemical change does the indicator undergo which causes it to change color, and, second, what is the cause of the characteristic differences in sensitiveness shown by such indicators as phenolphthaleïn and methyl orange towards the various acids and bases—differences which are of the greatest importance in laboratory practice.

Considering first the more interesting question as to the change of color, we find two distinct views held; but only one, the theory of Ostwald, has become generally known and has found a place

[1] See Stieglitz, this Journal, **24**, 588 (1902).

and uniform acceptance in every modern text-book examined[1] which discusses the subject at all.[2] It is extremely probable, moreover, that this theory is wrong in so far as the interpretation of the cause of the change of color is concerned. The other view, growing out of researches with organic dyes and other colored substances, appears to be almost unknown, although work in more recent years is confirming results which had their origin over ten years ago. While most likely wrong in regard to the one question of change of color, Ostwald, in his theory of indicators, has undoubtedly laid down correctly the guiding principles of the proper theoretical treatment of the second, scientifically far more important, question, concerning the varying sensitiveness of the indicators to acids and bases. In this paper, it is proposed to discuss, critically, the two theories concerning the change of color and particularly to develop the relation of the newer interpretation of this phenomenon to Ostwald's fundamental views on the sensitiveness of indicators. It is thought that such a development may remove the main obstacle in the way of the general acceptance of what seems to the author the correct explanation of the color change.

THE CHANGE OF COLOR OF INDICATORS.

The Ionization Theory.—All indicators used with acids and bases, as Ostwald pointed out, are themselves either bases or acids and capable of salt formation. A few, like methyl orange,[3] are at the same time both base and acid (amphoter), and able to form salts either with an acid or a base. There is an undoubted intimate connection between this salt formation and the change of color, but what is the real nature of the connection? According to Ostwald's theory,[4] which has found such wide acceptance, the change of color of an indicator, tersely expressed, is due to a change of its ionic condition. In the case of phenolphthaleïn, which may be used in illustration, the colorless molecule,

[1] Ostwald's "Lehrbuch der allgemeinen Chemie," 1891, and "Scientific Foundations of Analytical Chemistry," 1900; Walker's "Introduction to Physical Chemistry," 1899; Nernst's "Theoretische Chemie," 1900; Arrhenius's "Electrochemie," 1901; Jones's "Elements of Physical Chemistry," 1902, and "Principles of Inorganic Chemistry," 1903.

[2] See, however, W. A. Noyes's "Organic Chemistry," published while this paper was being written, and referring to the other, probably correct view.

[3] The indicator characteristics of methyl orange are due essentially to its basic character (see below).

[4] Ostwald: *Loc. cit.*

$OCOC_6H_4C(C_6H_4OH)_2$, (I), is supposed to produce the red negative ion, $\overline{O}COC_6H_4C(C_6H_4OH)C_6H_4\overline{O}$, (II). Phenolphthaleïn, which appears to be a very weak acid, can indeed be very little ionized in aqueous solution, and the dissociation constant for the condition of equilibrium,

$$PH \rightleftarrows P' + H^{\cdot},$$

must be so small that a slight excess of hydrogen ions from any acid would be able to suppress almost completely the negative phenolphthaleïn ions. Its alkali salts, however, would be very highly ionized, like all alkali salts. We have, therefore, coincident with the change of color, a change also of phenolphthaleïn from the molecular to the ionic condition. It was, perhaps, a perfectly natural, although not a necessary, conclusion that the simultaneous change of ionic condition and color bear the relation to each other of cause and effect. This conclusion was, doubtless, even more readily reached and accepted because Ostwald had just shown,[1] with the aid of the spectroscope, that many of the characteristic changes of color which dry inorganic salts experience on treatment with water are almost certainly due to changes from the molecular form to the differently colored ions, so that solutions of all salts of a given metal like copper show identical absorption spectra when the salts are completely ionized.[2] In spite of this parallel with inorganic salts and, notwithstanding the striking coincidence mentioned above, on which this theory of the change of color of an indicator like phenolphthaleïn is based, facts have been known for ten years and new ones have become known more recently, which prove that the change is not primarily due to a change of ionic condition, but to a very important change of constitution of the phenolphthaleïn molecule when it goes from the colorless into the red condition.

The "Chromophoric Theory."—In view of what chemists have known for over a quarter of a century about the intimate connection between color production and constitution of organic compounds, the explanation that phenolphthaleïn (I) without a single chromophoric group should become intensely red by forming the ion (II) without any chromophoric group, appeared from the

[1] In the "Lehrbuch," p. 799, the theory of indicators follows immediately the discussion of the color of inorganic salts.

[2] See, however, Kastle, *Am. Chem. J.*, **16**, 326 (1894).

outset as extremely unlikely. As early as 1892, a year after Ostwald's theory was published, Bernthsen[1] made it appear practically certain that whereas phenolphthaleïn in its colorless solution has the constitution of a lactone, as expressed by (I), its red salts are the salts of a carboxyl acid, not a phenol, and have the constitution.[2] $(MeOOC.C_6H_4)(HOC_6H_4)C:C_6H_4:O$. The strongly chromophoric quinoid complex $(:C_6H_4:O)$ gives us an explanation of the production of intense color, which is entirely adequate, in view of the general laws governing color in organic compounds. The sodium salt is, no doubt, incidentally ionized in solution, but that this ionization is merely a coincidence and not a cause is established by the fact that the solid, dry, non-ionized silver salt is also intensely colored (violet). Other strong proof that the view first presented by Bernthsen is the correct one, lies in the fact that Nietzki and Burckhart[3] have prepared colored, non-ionized ethers of tetrabromphenolphthaleïn,

$$(C_2H_5O_2C.C_6H_4)(HOC_6H_2Br_2).C:C_6H_2Br_2:O$$

and

$$(C_2H_5O_2C.C_6H_4)(C_2H_5OC_6H_2Br_2).C:C_6H_2Br_2:O,$$

with quinoid molecules, and colorless lactoid ethers, isomeric with the colored one, namely,

$$OCOC_6H_4C(C_6H_4Br_2OH)(C_6H_2Br_2OC_2H_5)$$

and

$$OCOC_6H_4C(C_6H_2Br_2OC_2H_5)_2.$$

In the absence of the chromophoric quinoid group, color is also absent, but the question of ionization has no effect at all on the matter of color or absence of color.

Similarly, it has long been known that the intensely colored salts of the rosaniline series of dyes are quinone derivatives, *e. g.*, the hydrochloride of pararosaniline,

$$(H_2NC_6H_4)_2C:C_6H_4:NH_2Cl,$$

and that the corresponding free base is more or less rapidly converted into the isomeric, colorless carbinol,

$$(H_2NC_6H_4)_3C(OH),$$

the color disappearing again with the quinone complex. The

[1] *Chem. Ztg.*, p. 1956 (1892). *Vide* also Friedländer: *Ber. d. chem. Ges.*, **26**, 172, 2258 (1893).

[2] The lactone ring is saponified very readily by alkalies, as are lactones in general.

[3] *Ber. d. chem. Ges.*, **30**, 175 (1897).

difference between the behavior of phenolphthaleïn and rosaniline, as will be shown, is essentially a difference in the speed of the change of constitution. More recently, Hantzsch[1] has shown that, in general, the change of colorless organic compounds into highly colored salts is invariably accompanied by a modification of the constitution affecting a chromophoric group. Reference need only be made to the formation of red salts,

$$RC(NO_2): NONa,$$

from the colorless nitrolic acid,

$$RCH(NO_2)NO.$$

THE CHANGE OF COLOR OF INDICATORS SHOWING TWO COLORS.

The Ionization Theory.—Turning to the consideration of a second kind of indicators, such as methyl orange and litmus, which change from one color to another, we again find the two theories confronting each other. According to Ostwald's views,[2] as slightly modified by Küster,[3] the yellow color of methyl orange in alkaline solution is due to the formation of an intensely yellow, negative ion,

$$\bar{O}_3SC_6H_4N:NC_6H_4N(CH_3)_2,$$

methyl orange, which is amphoter, behaving in this case as an acid. In acid solution, we have an ion which carries both a negative and a positive charge,

$$\bar{O}_3SC_6H_4N:NC_6H_4N(\dot{C}H_3)_2H,$$

and which is said to have a not very intense red color. The difference between the two colored substances is supposed to be simply one of ionization; both are supposed to have essentially the same chromophoric complex (the azo groups, N : N), but different electric charges.

The "Chromophoric Theory."—In view of what has been explained above as to the change of constitution and of chromophoric complexes attending the change of phenolphthaleïn, the rosanilines, etc., from a colorless to a colored condition, we are justified in questioning the adequateness of the ionization explanation of the change of color, also, of bicolored indicators like methyl orange. We may ask whether analogous, constitutional and chromophoric changes of the molecule of methyl orange do not

[1] *Ibid.*, **32**, 583, 3085 (1899), etc.

[2] "Scientific Foundations of Analytical Chemistry."

[3] *Ztschr. anorg. Chem.*, **13**, 135 (1897); *Vide* Bredig: *Ztschr. Elektrochem.*, **6**, 33 (1899).

accompany its transition from yellow to red, and vice versa. As a matter of fact, for reasons quite distinct from the sole question of color, chemists have for a number of years been seriously divided as to the true constitution of dyes of the class of methyl orange (amino and hydroxyazobenzene dyes). There are two possible constitutions for methyl orange:

(I) $HO_3SC_6H_4N:NC_6H_4N(CH_3)_2$

which represents an aminoazobenzene with a chromophoric azo group (N:N), and

(II) $O_3SC_6H_4NH.N:C_6H_4:N(CH_3)_2$,

the inner salt (sulphonate) of a phenylhydrazone of an iminoquinone, containing the chromophoric quinoid group ($:C_6H_4:$). It seems extremely probable that in alkaline solutions we have yellow, metal salts of methyl orange of the constitution (I), with the azo group, and, in acid solution, red salts of the quinoid constitution (II) or, in the presence of an excess of acid, the perfectly analogous red salts of other acids, such as

(II′) $HO_3SC_6H_4NH.N:C_6H_4:N(CH_3)_2Cl.$

The change of color would then be attended by a profound change of chromophoric complexes. Aside from the general considerations of analogy to phenolphthaleïn and other dyes, and of agreement with the general laws governing color in organic compounds, the chief support for this "chromophoric theory" of the change of color of bicolored indicators is found in the fact that for hydroxyazobenzene, which structurally is entirely analogous to methyl orange, Hantzsch[1] has recently proved that in alkaline solutions it is, indeed, the salt of an azophenol,

$$C_6H_5N:NC_6H_4ONa,$$

but in neutral and acid solutions a phenylhydrazone of quinone, *e. g.*,

$$(HClC_6H_5NH).N:C_6H_4:O.$$

The dry sodium salt is orange, the dry hydrochloride a deep purple-red. With the change of constitution we have, therefore, again a marked change of color.

THE CHANGE OF COLOR AND OF IONIZATION A COINCIDENCE.

Results of the last ten years in the field of organic chemical research, such as the work of Nef on the salts of acetoacetic and

[1] *Ber. d. chem. Ges.*, **32**, 590, 3089 (1899).

malonic ethers,[1] and of Hantzsch on pseudo-acids and bases, enable us to understand also very readily why there should be this striking coincidence between the change of color of indicators and the change of the ionic condition without any strictly causal relation between the two facts. The coincident is simply due to the fact that many organic acids, and among them indicators that are acids, are extremely unstable in the form of *free acids,* and readily suffer a change of constitution to closely allied, isomeric (tautomeric) substances, which are no true acids (not ionized). Analogous relations are known to exist for many organic bases. The *salts,* however, of such acids or bases are stable, whether in solution (ionized) or dry (non-ionized). Thus nitrophenylmethane is known in two forms;[2] isonitrophenylmethane,

$$C_6H_5CH:NOOH,$$

a rather strong acid, which is precipitated when the solutions of its salts are rapidly and strongly acidified, but which changes gradually and spontaneously to a stable, neutral isomer, nitrophenylmethane,

$$C_6H_5CH_2.NO_2.$$

In other cases of this kind, the isomerization is instantaneous.

Such a substance, to be serviceable as an indicator, must suffer isomerization from the acid (or basic) condition to the pseudo (neutral) condition or vice versa, practically *instantaneously* and the isomerization *must also affect a chromophoric group.* In the case of phenolphthalein, which may again serve in illustration, we must have a true acid form,

$$H^*OOCC_6H_4(HOC_6H_4)C:C_6H_4:O,$$

from which the colored metallic salts are derived, but which in

[1] Vorländer (*Ber. d. chem. Ges.*, **36**, 268 (1903)), having proved malonic ether to be a true weak acid in aqueous solution, supposed that this fact proves also that the salts of malonic ether have the constitution $MeCH(COOR)_2$ and not ROOC.CH : C(OMe)OR, as advocated by Nef. As a matter of fact, the evidence merely shows that malonic ether is somewhat ionized in aqueous solution and a very weak acid. The assumption that an oxygen acid, ROOC.CH : C(OH)OR, must be a strong acid is entirely unwarranted ; but, moreover, the important fact is left entirely out of consideration that in an aqueous solution, two forms of malonic ether would be in equilibrium with each other, *viz.*,

$$ROOC.CH_2COOR \rightleftarrows ROOC.CH:C(OH)OR.$$

If there were very little of the latter acid found present, malonic acid would appear to be a very weak acid, even if the acid form ionized quite easily (see below). The results of Vorländer are, therefore, evidence neither for nor against Nef's views as to the constitution of the salts, and taken in connection with Hantzsch's work on pseudo-acids rather confirm Nef's conclusions.

[2] Hantsch : *Ber. d. chem. Ges.*, **29**, 699, 2251 (1896).

the free acid condition must go, practically, instantly over into the colorless lactoid form,

$$\underset{\llcorner_____\lrcorner}{OOCC_6H_4C(C_6H_4OH)_2},^1$$

the hydrogen atom, H*, suffering a change of position. The lactone is the more stable of the two isomers, belonging, as it does, to the most stable class of lactones, the γ-lactones. However, in an aqueous solution of phenolphthaleïn we must have, as in the case of all such tautomeric substances, a condition of equilibrium between the lactoid and quinoid forms:

$$\underset{\llcorner_____\lrcorner}{OCOC_6H_4C(C_6H_4OH)_2} \rightleftarrows HOOCC_6H_4C(C_6H_4OH):C_6H_4:O \quad (1)$$

The condition of equilibrium favors the lactoid form, since the solution is colorless, and only minimal quantities of the quinoid acid can be present. This trace of quinoid acid is ionized and in equilibrium with its ions:

$$HOOCC_6H_4C(C_6H_4OH):C_6H_4:O \rightleftarrows H^{\cdot} + \bar{O}OCC_6H_4C(C_6H_4OH):C_6H_4:O \quad (2)$$

The addition of an alkali causes the hydrogen ions (equation 2) to disappear; more of the quinoid molecules (equations 1 and 2) must be ionized to preserve equilibrium and the quinoid molecules, in turn, be reproduced from the lactoid (equation 1) as fast as the former are converted into the salt. The effect of the alkali, therefore, is to suppress the colorless lactoid isomer by converting the unstable, free quinoid acid into its stable quinoid salt, which is colored red and is incidentally ionized. That it is only a question of stability of the salt and not of ionization is proved by the fact that the dry salts are as intensely colored as the solution. The case is obviously entirely analogous to that of carbonic acid, whose neutral alkali salts, the carbonates, whether ionized in solution, or non-ionized in a dry state, are so very much more stable than the free acid. In fact, in both cases, the dry, non-ionized condition is rather more favorable to stability and, therefore, in the case of phenolphthaleïn, to the maximum formation of color, since in consequence of the ionization in aqueous solution we have hydrolysis and a reversal of equations (1) and

[1] It is possible that the unstable isomer, the true carboxylic acid, will some day be isolated; but this is not at all essential for the theory, as analogous unstable isomers, such as isonitrophenylmethane, have been isolated and their spontaneous change studied.

(2) for phenolphthaleïn and an analogous change of the carbonates.

The equilibrium equations (1) and (2), as just developed, enable us to put the two theories of the cause of the change of color of indicators briefly, thus: Ostwald's theory takes an equation analogous to (2), *viz.*,

$$\underset{\text{(Colorless)}}{OCOC_6H_4C(C_6H_4OH)_2} \rightleftarrows H^{\cdot} + \underset{\text{(Red)}}{OCOC_6H_4C(C_6H_4OH)(C_6H_4\bar{O})} \quad (2'),$$

alone into account, ascribing the change of color to the shifting of equilibrium according to (2'); the "chromophoric theory" takes both equations, (1) and (2), into account and ascribes the *change* of *color* to the shifting of equilibrium according to (1).

THE SENSITIVENESS OF INDICATORS.

This condensed contrast of the two theories enables us to proceed to the second question raised in the opening paragraph of this paper, to the question as to the different degrees of sensitiveness of the various indicators to weak acids and bases.

In this, the more important of the two questions raised, Ostwald has brilliantly laid the foundations for a correct theoretical interpretation and practical application of the varying phenomena, and we need only consider in what relation the new interpretation of the cause of the change of color stands to his views on the sensitiveness of indicators.

The Ionization Theory.—According to Ostwald, the indicators, as acids and bases, take part in the changes of chemical equilibrium in the solution by forming salts and are subject to the general laws governing equilibrium and notably to that of mass action. The sensitiveness of an indicator, consequently, must depend chiefly on the numerical size of its ionization constant as an acid or base. For instance, according to (2')

$$C_H \times C_L = K \times C_{LH}, \qquad (3)$$

if C_H, C_L, and C_{LH} represent, respectively, the concentrations of the hydrogen ions, the complex organic negative ions and the non-ionized molecules of an acid indicator, and K its ionization constant according to Ostwald's dilution law for organic acids. If, as in the case of phenolphthaleïn, the colored substance is the complex negative ion, the formation and intensity of color would

be measured by C_L. As explained above, by the suppression of the hydrogen ions (C_H) and the formation of metal salts, which are largely ionized, C_L would become very large. Now, if the ionization constant K is exceedingly small and the indicator, therefore, a very weak acid, it cannot be sensitive to very weak bases, because the nearer the dissociation constants of base and acid approach that of water itself, the less readily are salts formed; water prevents their formation by hydrolysis according to the well-known equation:

$$\overset{+}{Me} + \overset{-}{L} + H_2O \rightarrow LH + MeOH. \qquad (4)$$

In the same way, the smaller the dissociation constant K or the weaker the indicator is as an acid, the more sensitive and, therefore, the more serviceable will it be in the titration of ordinarily weak acids, such as oxalic, acetic and carbonic; the small excess of hydrogen ions formed by these acids would be sufficient to drive the indicator out of its colored salts into the colorless molecules, since C_L grows smaller, according to (3), as C_H grows larger, and it does so the more rapidly the smaller K is.

By the same process of reasoning, it would follow, vice versa, that an indicator which is a moderately strong acid with a large dissociation constant, as methyl orange was supposed to be, or one which is a very weak base, with a very small dissociation constant as a base, as methyl orange really is,[1] would be an excellent indicator for strong or weak bases, but a very poor one for weak acids.

These conclusions, as developed from Ostwald's statements, agree in the main with the facts as far as they are known. Observations have been chiefly of a qualitative nature, and quantitative measurements of the dissociation constants of our most important indicators are extremely desirable,[2] but there is no reason to expect that they will modify in any way Ostwald's views which have just been described.

The "Chromophoric Theory."—The above views are based, however, on Ostwald's theory as to the change of color, briefly, for phenolphthaleïn, on equation (2′). But it is almost certain that this part of the theory is wrong and that the two equations, (1) and (2), express the changes in an indicator, and (1) in par-

[1] As explained below, the value of methyl orange as an indicator is due rather to its weak basic functions than to its acid character.

[2] *Vide* Bredig: *Loc. cit.*

ticular expresses the cause of the change of color. A brief consideration will show that this new view does not modify, in any fundamental respect, the result of the application of the laws of chemical equilibrium to the indicators, but simply introduces one or more new constant factors into the final equilibrium equation, factors which are rather helpful than otherwise in the interpretation of the facts.

Using phenolphthalein again as an illustration, we have two conditions of equilibrium occurring simultaneously in solution. First, according to equation (1), (p. 1119),

$$C_{QH} = k \times C_{LH}, \qquad (5)$$

if C_{LH} and C_{QH} represent the concentrations of the lactoid and quinoid forms of phenolphthaleïn and k is a constant. Again for equation (2), (p. 1119), we have

$$C_Q \times C_H = K' \times C_{QH}, \qquad (6)$$

if we express the concentrations of the negative quinoid ions and of the hydrogen ions by C_Q and C_H, that of the undissociated quinoid molecules again by C_{QH}, and the ionization constant of Ostwald's dilution law by K′.

Combining (5) and (6) we have:

$$C_Q \times C_H = k \times K' \times C_{LH} \qquad (7)$$

or

$$C_Q \times C_H = K'' \times C_{LH}. \qquad (7')^1$$

This is the same form of equation as developed above for the sensitiveness of the indicators (equation 3), with this simple difference that in equation (3) the constant K is only the ionization constant, in equation (7′), K″ is the product of the true ionization constant K′ of the quinoid acid and the stability constant k of the two tautomeric forms of phenolphthaleïn. Equation (7′) tells us, therefore, that such an acid as phenolphthaleïn is in its effect only as strong an acid as the joint action of ionization and possibility of molecular existence in solution make it. Its tend-

[1] In this expression, for an aqueous solution of phenolphthaleïn, C_Q and C_H are not equal to each other, as hydrogen ions are formed not only by the carboxyl group of the quinoid acid but also by its phenolhydroxyl group as well as by the two phenolhydroxyl groups of the lactoid acid. The effect of this increase of hydrogen ions is to make phenolphthaleïn, as indicator, react as a still weaker acid than it otherwise would, that is, it is less sensitive to alkalies, more sensitive to acids. Thus phenolphthaleïn is affected favorably in the very direction in which it is of particular value as an indicator. A most instructive quantitative study of similar relations has been carried out for carbonic acid by H. N. McCoy, *Am. Chem. J.*, **29**, 437 (1903).

ency to produce the red color is measured by the same constant K''. Entirely analogous relations and equilibrium equations, it may be added, exist for ammonium hydroxide, which also is unstable in solution.[1]

It is obvious from a comparison of equations (7') and (3), that all of the conclusions as to sensitiveness which were based on equation (3) apply equally well to the new equation (7'). The substitution of (7) for (3) shows us further, however, the great importance of the stability constant k, for the smaller k is the more difficult will it be to obtain the quinoid acid and its salts, to which the red color of the alkaline phenolphthaleïn solution is due, and consequently the less sensitive will the indicator be to alkalies. It is very probable, indeed, that phenolphthaleïn in its quinoid form with a carboxyl group is not such a very weak acid in itself, but the minute quantities in which it is able to exist in the free state make it appear and react as such.

But a still more important conclusion concerning indicators can be drawn from the substitution of equation (7') for (3) and the introduction of the stability constant k into the final equilibrium equation. Whereas changes involving only new conditions of equilibrium of ions always take place practically instantaneously (equation 6), reactions involving the transformation of one isomer into another (equation 5) show the widest range of difference as regards the velocities of the changes. The constant k of this equation (5), as is well known, is merely the ratio of the velocities of the two opposite reactions; the same ratio may be the result of two exceedingly great or two very small velocities. Now the velocities of change for serviceable indicators, no matter what their ratio is, must be exceedingly great in either direction, and practically of the order of the velocity of ionic changes. It is very probable that in the case of the indicators actually used the velocities are not only very great in both directions, but are increased by the catalytic action of hydroxyl and hydrogen ions[1] in such a way that complete equilibrium, according to (5) and (6), is reached instantaneously. This consideration shows us wherein an indicator differs from other intensely colored sub-

[1] Kohlrausch: Wied. *Ann*., **26**, 197 (1885); Ostwald: *J. prakt. Chem.* (2), **33**, 358 (1886), and *Ztschr. phys. Chem.*, **2**, 36 (1888); Hantzsch: *Ibid.*, **30**, 258 (1899).

[2] Cameron's observation (*Am. Chem. J.*, **23**, 477 (1900)) that the red color of phenolphthaleïn is rather slowly discharged by carbonic acid may be the result of such an action. His own interpretation is surely wrong.

stances, such as rosaniline, which shows as striking color changes as phenolphthaleïn; it is intensely red in solution, colorless (as carbinol) in alkaline solution, but the transformations are much too slow,[1] at ordinary temperatures, to make rosonaline available as an indicator in acidimetry.[2]

For methyl orange, which exhibits a sensitiveness in extreme contrast to that of phenolphthaleïn and which, incidentally, is a bicolored indicator, relations exist which are entirely analogous to those developed above for phenolphthaleïn. It is always used in neutral solution in the form of a sodium salt and it is in this sensitive neutral solution that we must have a condition of equilibrium between the two tautomeric forms of methyl orange, which were previously discussed (p. 1117). It can best be expressed as follows:[3]

$$\begin{matrix} SO_3C_6H_4N:NC_6H_4N(CH_3)_2HOH \rightleftarrows \\ SO_3C_6H_4NH.N:C_6H_4:N(CH_3)_2OH, \end{matrix} \qquad (8)$$

or

$$AzOH \rightleftarrows QOH.$$

The azo derivative on the left hand of the equation is yellow, as the solid sodium salt, which can only be

$$NaSO_3C_6H_4N:NC_6H_4N(CH_3)_2,$$

is yellow; the quinoid form on the right hand is red, for instance, in the form of the solid free sulphonate,

$$SO_3.C_6H_4NH.N:C_6H_4N(CH_3)_2,$$

as explained above.

[1] It is also too strong a base to be very sensitive.

[2] NOTE.—In his work on the pseudo-acids and -bases, Hantzsch uses the method of comparing the affinity constant, for instance, of an acid as determined from the measurement of the hydrolysis of its salt, with the affinity constant as ascertained by conductivity measurements in the aqueous solution of the pseudo-acid and decides, on the basis of the great differences in the values obtained, that the free acid must be a different substance (isomeric or tautomeric) from the acid in the salt. This conclusion is perfectly justified and the method an admirable one. But it is never clearly emphasized by Hantzsch—perhaps inadvertently—that such differences can result only if measurements are made before a final condition of equilibrium can possibly have been reached in all the solutions used. Equation (7′), as used in the text, rests, therefore, less on quantitative work done with tautomeric substances than on the experimental work of Kohlrausch (*Loc. cit.*) and Ostwald (*Loc. cit.*) on the ionization of ammonium hydroxide and on that of Bodländer (*Ztschr. phys. Chem.*, **35**, 32) and McCoy (*Loc. cit.*) on carbonic acid as well as on the laws of chemical equilibrium.

[3] The sulphonate group, SO_3Na, is ionized and has absolutely nothing to do with the color changes, as was at first supposed; dimethylaminoazobenzene may be used in place of its sulphuric acid derivative, methyl orange. *Vide* Bredig: *Loc. cit.*

If we represent the concentrations in the usual way, we obtain from (8) the equilibrium equation

$$k \times C_{AzOH} = C_{QOH}. \qquad (9)$$

As the solution is yellow, the second quinoid form can only be present in very small quantities and the stability constant k must be exceedingly small.

The red quinoid form is also ionized as an ammonium base, according to

$$QOH \rightleftarrows \overset{+}{Q} + \overset{-}{O}H. \qquad (10)$$

We have, then,

$$C_Q \times C_{OH} = K \times C_{QOH}, \qquad (11)$$

and combining (9) and (11),

$$C_Q \times C_{OH} = k \times K \times C_{AzOH}, \qquad (12)$$

$$C_Q \times C_{OH} = K' \times C_{AzOH}. \qquad (12')$$[1]

This is the same form of equation as was developed above for phenolphthaleïn (equation 7 and 7′), only we are dealing in this case with a base rather than with an acid. The ion Q and its salts are red and the red color of the acid methyl orange solution depends on the presence of Q and its development is subject to the equilibrium equation (12) or (12′).

The whole behavior of the red, quinoid form of methyl orange (its sodium salt) is that of a *very weak* base, analogous to that of dimethylaminoazobenzene[2] or to the sodium salt of amino-acetic acid.[3] It does not form salts readily with weak acids, such as carbonic and acetic acids; the red carbonate,

$$(NaSO_3.C_6H_4NH.N:C_6H_4:N(CH_3)_2)_2CO_3,$$

is practically completely hydrolyzed and incapable of existence, the liberated base reverting, according to (8) and (9), to the stable yellow isomer. That is why methyl orange is not a sensitive indicator for weak acids. As a very weak base, it will be driven readily out of its red salts by other bases, even weak ones, and the free, red base will revert again, according to (8) and (9), to the yellow form, the result being that methyl orange is an ex-

[1] As the amino group of the azo form is basic and forms some hydroxyl ions, C_{OH} is somewhat larger than C_Q in an aqueous solution. This fact, in the same way as explained above for phenolphthaleïn, favors the sensitiveness of methyl orange to weak bases, its most important characteristic.

[2] Bredig: *Loc. cit.* *Vide*, however, Ostwald: *Loc. cit.*, and Küster: *Loc. cit.*

[3] Lengfeld and Stieglitz: *Am. Chem. J.*, **15**, 516 (1893).

cellent sensitive indicator for weak bases. Accordingly, K′, of equation (12′), must have a very small value, of the order of K″ for phenolphthaleïn in equation (7′). As the ionization constant K (equation 11) of the quaternary ammonium hydroxide must be a rather large one, the very small value of K′ is evidently due to the exceedingly small size of the stability constant *k*, which is shown, qualitatively at least, by the color of the neutral methyl orange solution.

Our two most valuable indicators, phenolphthaleïn and methyl orange, which form an extreme contrast, do so as a very weak acid and a very weak base, respectively, in their *quinoid* (red) forms, as shown in equations (7′) and (12′); and their weakness is due in largest measure to the *instability* of the quinoid isomers in the form of free acid or free base, respectively.

These considerations give us a complete survey of the chemistry of the different sensitiveness of our two most important indicators on the basis of the conclusions reached in the first part of this paper that the color change must be primarily due to a change of constitution involving a chromophoric complex. An experimental determination of the constants and verification of these views would be very important.[1] They rest, so far, on the work of Bernthsen, Nietzki, and Burckhardt on the phenolphthaleïns; on Hantzsch's investigation of the pseudo-acids and -bases, and on the quantitative study of the equilibrium conditions of ammonium hydroxide and of carbonic acid in solution, as quoted above. An experimental study of the peculiarities of indicators, such as the disappearance of the color of phenolphthaleïn in the presence of a large excess of alkali, would also be profitable and the quinone complex, with its well-known reactivity, would probably be found to be the seat also of this change.[2]

In conclusion, in connection with the discussion of the sensitiveness of our indicators, too much emphasis cannot be laid on the fact that the lack of sensitiveness of phenolphthaleïn in laboratory practice in the titration of a weak base like ammonia or of methyl orange in the titration of a weak acid like acetic acid is

[1] Bredig (*Loc. cit.*) has announced an experimental study of methyl orange from Ostwald's point of view, and Dr. H. N. McCoy, of this laboratory, in connection with his work on the affinity constants of carbonic acid, has taken up the determination of the affinity constant of phenolphthaleïn. The author feels obliged to refrain from pursuing his subject experimentally until these researches are completed.

[2] The colorless solution probably contains the salt $KO_2C.C_6H_4C(OH)(C_6H_4OK)_2$. The corresponding triacetate of aurine, $C(OH)(C_6H_4OC_2H_3O)_3$, is known and is colorless.

ultimately due chiefly to the fact that a weak base or a weak acid is very much weaker (less ionized) in the presence of its own salts than in pure aqueous solutions.[1] Phenolphthaleïn will readily show the presence of 0.01 cc. N/10 free ammonia in 100 cc. of pure boiled water, to which only 1 milligram of phenolphthaleïn has been added. But in titrating ammonia with N/10 hydrochloric acid, very long before all but that small amount has been neutralized, the red color of phenolphthaleïn disappears, owing to the formation of ammonium chloride. The isothermic equation for ammonium hydroxide is

$$C_{NH_4} \times C_{OH} = k \times C_{NH_3},$$

in which C_{NH_4}, C_{OH}, C_{NH_3} represent the concentrations of the ammonium ions, the hydroxyl ions and the non-ionized ammonia, and k $(= 1 : 53{,}750)$[2] is the ionization constant. It shows how readily the hydroxyl ions must disappear when an easily ionized salt like ammonium chloride is added to a solution of ammonia. A striking insight into the matter is obtained from the result of the following calculation, made with the aid of the isothermic equation and its known constant and of the known degrees of dissociation of solutions of ammonium chloride: If 10 cc. normal ammonium hydroxide are half neutralized by 5 cc. normal hydrochloric acid, the resulting solution, instead of being one-half as effective as a base, as it would have been if sodium hydroxide had been used, contains very nearly only one-hundredth as many hydroxyl ions as the original solution and is, therefore, only one-hundredth as effective as a base. The same result would be attained if to 10 cc. normal ammonium hydroxide 0.32 gram solid ammonium chloride $(= 6$ cc. normal ammonium chloride$)$ is added in place of all the acid. In other words, in these concentrations ammonia is weakened fifty times more by the neutral salt ammonium chloride than by the hydrogen ions (in their neutralizing effect) of a nearly equivalent[3] amount of hydrochloric acid. Analogous relations hold for the neutralizing of acetic acid by sodium hydroxide, the affinity constant of acetic acid $(1 : 55{,}000)$ being nearly the same as that of ammonia.

[1] Arrhenius: *Ztschr. phys. Chem.*, **2**, 287 (1888); Küster: *Ztschr. Elektrochem.*, **4**, 110 (1897); Stieglitz: *Am. Chem. J.*, **23**, 406 (1900).

[2] Kohlrausch: *Loc. cit.*; Ostwald: *Loc. cit.*

[3] Equivalent to the ammonium chloride.

CHICAGO, April, 1903.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 76.]

THE BEHAVIOR OF CERIUM, LANTHANUM, NEODYMIUM, PRASEODYMIUM, THORIUM AND ZIRCONIUM TOWARD ORGANIC BASES.[1]

BY BURT LAWS HARTWELL.

Received August 18, 1903.

AN INVESTIGATION along these lines seemed to promise well because of the success which Jefferson[2] met while prosecuting a similar study with a limited number of aromatic bases. It was hoped that some organic base would be found, among the large number to be tried, which would lead to the separation of thorium and zirconium, or, failing in this, that a method would be disclosed by which these two elements could be separated from cerium, lanthanum, neodymium and praseodymium.

Large quantities of thorium and zirconium nitrates were prepared from the mineral thorite and zircon. Numerous qualitative tests were made and the solvents for the bases were, in most cases, water and alcohol, or mixtures of these two, depending upon the solubility of the base. In some instances ether was added to advantage. Alcohol, above a certain strength, precipitated the thorium and zirconium nitrate solutions, so that this point had to be constantly considered during the testing. The salt solution was usually added in small quantities at a time to the solution containing a liberal amount of the organic base. Heat was applied, if precipitation did not occur in the cold. The solutions were not permitted to stand for long periods, as it was thought that differences which did not manifest themselves readily, under ordinary conditions, would scarcely indicate the probability of practical quantitative separations.

The bases studied in this investigation were obtained from Kahlbaum. Those employed by Jefferson[3] were usually omitted here.

REAGENTS WHICH PRODUCED NO PRECIPITATE WITH SALTS OF ANY ONE OF THE SIX ELEMENTS.

Benzylaniline.	***p*-Nitraniline.**
Dimethylnitrosamine.	***p*-Nitrophenylhydrazine.**

[1] From author's thesis for the Ph.D. degree.

[2] This Journal, **24**, 540.

[3] *Loc. cit.*

Dipropylnitrosamine.
m-Nitraniline.
o-Nitraniline.
o-Chloraniline.
Piperine.
Succinimide.
Tetranitromethylaniline.

REAGENTS WHICH CAUSED PRECIPITATES WITH SALTS OF ALL SIX OF THE ELEMENTS.

Allylamine.
Benzylmethylamine.
Bornylamine.
Camphylamine.
Diamylamine.
Dibenzylamine.
Diethylamine.
Dimethylamine.
Dipropylamine.
Ethylenediamine.
Heptylamine.
Hexylamine.
Isobutylamine.
Isotributylamine.
Isodibutylamine.
Monoamylamine.
Monethylamine.
Monomethylamine.
Monopropylamine.
Neurine.
Normal butylamine.
Normaldibutylamine.
Propylenediamine.
Tetrethylammonium hydroxide.
Tetramethylammonium hydroxide.
Triethylamine.
Trimethylamine.
Tripropylamine.

REAGENTS WHICH PRECIPITATED ONLY THORIUM AND ZIRCONIUM.

Benzidine.
m-Bromaniline.
p-Bromaniline.
p-Bromphenylhydrazine.
p-Chloraniline.
Isoquinoline.
α-Picoline.
p-Toluidine.
m-Toluylenediamine.
Tribenzylamine.

REAGENTS NOT INCLUDED IN THE PRECEDING GROUPS AND WHOSE REACTIONS ARE MENTIONED UPON SUCCEEDING PAGES.

m-Chloraniline.
Diethylaniline.
Hexamethylenetetramine.
Monethylaniline.
Monomethylaniline.
α-Naphthylamine.
β-Naphthylamine.
Tetrahydroquinoline.
m-Toluidine.
o-Xylidine.
p-Xylidine.

The bases of the first and second groups were manifestly unsuited for the purpose in mind. Those of the third and fourth groups showing differences in deportment with the several elements under consideration were given more particular attention, while those which were insoluble in dilute alcoholic solutions were placed to one side. The following paragraphs record the observations made with the several bodies which seemed best adapted for quantitative separations.

[1] *Loc. cit.*

Thorium and Zirconium with the Chloranilines.—The different behaviors of the chloranilines substantiate the views held regarding their relative basicity.[1] *o*-Chloraniline did not precipitate thorium or zirconium. *m*-Chloraniline precipitated zirconium in the cold, but with thorium, heat was required to produce precipitation, while *p*-chloraniline precipitated the solutions of both elements, even in the cold. Solutions of cerium, lanthanum, neodymium and praseodymium salts were not affected by these reagents.

Zirconium and Thorium with m-Chloraniline.—Much work was done upon *m*-chloraniline to arrive at the proper conditions in the strength of alcohol and temperature favorable to the complete precipitation of the zirconium solutions, and at the same time to leave the thorium salt unprecipitated. A solution containing equal parts of water and commercial alcohol was found most satisfactory. At a temperature of 60°-70°, this solvent containing *m*-chloraniline occasioned no precipitation in solutions of thorium nitrate, while in zirconium nitrate solutions it precipitated 0.0995 gram, 0.0988 gram, 0.0990 gram and 0.0988 gram of zirconium oxide, instead of 0.0995 gram obtained by ammonia or 0.0993 gram by direct evaporation and ignition. On repeating the experiment with a mixture of the thorium and zirconium nitrates, both elements were completely precipitated.

Thorium and Zirconium with Hexamethylenetetramine (Formin).—Formin in the qualitative tests showed a marked difference in behavior. Thus a thorium solution, after its addition, stood forty-two hours at room temperature without the appearance of a precipitate. Upon adding the zirconium nitrate solution, both hydroxides were precipitated completely.

α- and β-Naphthylamine, *m*-bromaniline and *p*-bromphenylhydrazine precipitated zirconium solutions much more completely than those of thorium, but separations could not be effected by means of them. They reacted indifferently with the salts of cerium, lanthanum, neodymium and praseodymium. *o*-Bromaniline was not tried at all in this investigation.

In a solution of the nitrates of zirconium and cerium, *m*-chloraniline precipitated 0.0532 gram of zirconium oxide, instead of 0.0539 gram obtained with ammonia water. *p*-Chloraniline precipitated 0.0536 gram, *m*-bromaniline 0.0524 gram, and β-naph-

[1] Van't Hoff's "Lectures on Theoretical and Physical Chemistry," Vol. II, p. 102.

thylamine 0.0533 gram. In the first three filtrates 0.0396 gram, 0.0400 gram and 0.0396 gram, respectively, of cerium oxide were obtained, instead of the theoretical 0.0389 gram. In using *p*-chloraniline with a solution containing twice the quantities of zirconium and cerium oxide given above, a very satisfactory quantitative separation resulted.

In precipitating a mixture of zirconium and cerium salts with *p*-toluidine, 0.1341 gram of zirconium oxide was found, while the theoretical amount present was 0.1347 gram. This same reagent added to a solution of thorium and cerium nitrates precipitated 0.1246 gram, 0.1236 gram and 0.1261 gram, instead of 0.1247 gram.

While monomethylaniline precipitated cerium solutions completely and apparently had no marked effect upon those of lanthanum, neodymium and praseodymium, the attempts at quantitative separations were fruitless. Diethylaniline precipitated cerium salts quite completely. The insolubility, however, of this reagent compelled the use of such large amounts of alcohol that serious difficulties arose. These were not overcome. A quantitative separation of cerium from lanthanum was made by means of tetrahydroquinoline. Two precipitations of the cerium were necessary.

o- and *p*-Xylidine, as well as monethylaniline, precipitated cerium completely from its salt solutions. *m*-Toluidine seemed inadequate for this purpose.

p-Toluidine.—From observations made in the qualitative way, it appeared not improbable that *p*-toluidine might be employed to separate zirconium and thorium from lanthanum, neodymium and praseodymium. Accordingly, determinations were made in about 100 cc. of the weak alcoholic solutions, a moderate heat being applied to hasten the reaction. The precipitates formed were quite voluminous and somewhat gelatinous, especially in the case of zirconium, and well adapted for bringing down the accompanying element. On this account one reprecipitation was carried out in each case. The first precipitates dissolved readily in dilute nitric acid, especially if the solutions in the case of zirconium were not allowed to become too warm. The accompanying element was precipitated by ammonia from the combined filtrates. The ignition of the precipitates was conducted with free access of air, in

a porcelain crucible usually, and the blast-lamp used till constant weights were obtained. All of the weights, recorded in grams, are given in the condensed form below. The weights given as "required" were obtained by direct precipitation of the elements, separately, and blasting to constant weight, and represent the average of two closely agreeing results. The "combined" oxides represent the sum of the individual oxides. The results obtained in many cases do not agree well with the standard, but it was thought best to include all which, so far as known, were carried through without accident. Some minor differences in manipulation, such as varying the strength of alcohol, time of digestion, temperature, and volume of solution, were made in different cases. These variations may have influenced the results in some instances.

ZIRCONIUM AND LANTHANUM.

Zirconium oxide.		Lanthanum oxide.		Combined oxides.	
Found	Required.	Found.	Required.	Found.	Required.
0.1342	0.1341	0.0399	0.0409	0.1741	0.1750
0.1301	0.1341	0.0993	0.1023	0.2294	0.2364
0.1314	0.1341	0.1025	0.1023	0 2339	0.2364
0.1367	0.1341	0.0954	0.1023	0.2321	0.2364

ZIRCONIUM AND NEODYMIUM.

Zirconium oxide.		Neodymium oxide.		Combined oxides.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1349	0.1341	0.0413	0.0457	0.1762	0.1798
0.1439	0.1341	0.0973	0.1142	0.2412	0.2487
0.1372	0.1341	0.1102	0.1142	0.2474	0.2487
0.1446	0.1341	0.0952	0.1142	0.2398	0.2487

ZIRCONIUM AND PRASEODYMIUM.

Zirconium oxide.		Praseodymium oxide.		Combined oxides.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1317	0.1341	0.0420	0.0458	0.1737	0.1799
0.1344	0 1341	0.1099	0.1144	0.2443	0.2485
0.1312	0.1341	0.1129	0.1144	0.2441	0.2485
0.1304	0.1341	0.1014	0.1144	0.2318	0.2485

THORIUM AND LANTHANUM.

Thorium oxide.		Lanthanum oxide.		Combined oxides.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1254	0.1247	0.0407	0.0409	0.1661	0.1656
0.1222	0.1247	not det.	0.1023	.....	.....
0.1246	0.1247	0.1035	0.1023	0.2281	0.2270
0.1243	0.1247	0.1034	0.1023	0.2277	0.2270

THORIUM AND NEODYMIUM.

Thorium oxide.		Neodymium oxide.		Combined oxides	
Found.	Required.	Found.	Required.	Found.	Required.
0.1254	0.1247	0.0464	0.0457	0.1718	0.1704
0.1232	0.1247	0.1146	0.1142	0.2378	0.2389
0.1242	0.1247	0.1142	0.1142	0.2384	0.2389
0.1242	0.1247	0.1129	0.1142	0.2371	0.2389
0.1248	0.1247	0.1118	0.1142	0.2366	0 2389

THORIUM AND PRASEODYMIUM.

Thorium oxide.		Praseodymium oxide.		Combined oxide.	
Found.	Required.	Found.	Required.	Found.	Required.
0.1253	0.1247	0.0471	0.0458	0.1724	0.1705
0.1214	0.1247	0.1147	0.1144	0.2361	0.2391
0.1238	0.1247	0.1160	0.1144	0.2398	0.2391
0.1246	0.1247	not det.	0.1144	.....	.....

It will be noticed that the results with zirconium are not so satisfactory as those with thorium. This cannot be attributed to any difference in manipulation for they were obtained under similar conditions, the usual practice being to carry on the six separations at one time.

A tendency on the part of zirconium to resist separation from other elements is again indicated here. This tendency is exhibited by its precipitation being retarded by the presence of another element, and by the fact that when once brought down it frequently is contaminated by that element. In the attempts to separate zirconium from thorium by *m*-chloraniline, it was repeatedly noticed that conditions of digestion, sufficient to cause precipitation of zirconium by itself, were inadequate when thorium was present, and when the precipitate was thrown down it was badly contaminated with thorium. Similar observations were made when formin was used to effect their separation; in that case all of the thorium came down with the zirconium under conditions which failed to precipitate thorium when alone. It might be supposed that this peculiar behavior of zirconium would not be noticed upon passing from thorium to the more basic elements, but a number of the results obtained in connection with lanthanum and praseodymium show incomplete precipitations of zirconium, while neodymium was so inclined to come down with zirconium that a satisfactory separation could only be expected when all possible precautions had been taken to prevent it.

The oxides obtained by ammonia from the filtrates weighed less in the separations from zirconium than in those from thorium. If one attempts to attribute this difference to the greater solvent action of the filtrates from the zirconium, the only respect that suggests itself in which the two sets of filtrates differed is that they probably contained different amounts of the precipitant, *p*-toluidine. More of this reagent was necessary to effect a precipitation in the solutions containing thorium than in those in which zirconium was present, and it is probable that in carrying out the two precipitations, as was done in each instance, considerably more *p*-toluidine accumulated in the filtrates from the thorium. Sufficient attention was not given to this point while the determinations were being made to warrant an opinion as to the extent of its influence and it is merely offered as a possible explanation. As both the first and second precipitations were usually made from about 100 cc. of solution, the combined filtrates and washings, in which the precipitations by ammonia were made, were of considerable volume, and the question of the solvent effect of all this solution upon the precipitate produced by ammonia presented itself at the time of the determinations. The final filtrates were usually partially distilled, the bulk of the alcohol and ammonia being obtained in the distillate, from which the alcohol was recovered. More ammonia was repeatedly added to the undistilled portions to see if further precipitation would take place. In a few instances the entire solution was evaporated to dryness and the residue ignited and weighed. The weights obtained substantially made good the discrepancies between the combined oxides "obtained" and "required," but as no blank determinations were made it was not proved that some of this may not have come from extraneous sources.

As previously stated, the recorded results were obtained by the use of the blast-lamp till practically constant weights resulted. The writer is of the opinion, however, that errors may have occurred in this connection due to a constant composition not always being obtained, especially with lanthanum, neodymium and praseodymium. The weights obtained, by blasting the first two, were frequently 10 per cent. lower than those obtained by igniting over a Bunsen burner; there was less difference with praseodymium. Hitchcock[1] found that neodymium and praseodymium sesquioxides, by gentle ignition with free air access,

[1] This Journal, **17**, 525.

gradually took on oxygen till the weights approximated those represented by the formula M_2O_7.

Herzfeld[1] speaks of neodymium oxide as having a blue color and assigns to it the composition Nd_2O_3, and again,[2] in an abstract from Shapleigh's investigation, mentions a suboxide as a gray powder and a peroxide as a dirty gray powder. The oxide obtained in the present investigation was invariably of a light brown color resembling cocoa powder, after ignition with the Bunsen burner, and was usually changed to a light blue or light purple color by blasting. It was often necessary to pulverize and blast a long time before the bluish color was uniformly obtained; indeed, in some instances part of the oxide still retained the cocoa color even though by excessive blasting practically no change in weight resulted. In view of the inadequate and somewhat conflicting information concerning neodymium oxides, the composition of the oxide obtained in any particular case must receive careful attention. The change of color produced by blasting the lanthanum and praseodymium oxides was not sufficient to indicate a change in composition, but the weights, especially with lanthanum, were considerably reduced and the certainty of a definite composition should also be established in this instance.

The most that was attempted, during the present work, with any of the oxides, was to compare the weights obtained in the course of the analyses with those obtained by direct precipitation from the aqueous solutions by ammonia, and blasting until they were constant within a few tenths of a milligram. It would seem as though the oxides obtained in this manner would be of constant composition, but it is not improbable that small variations may have occurred and that lack of nice conformity may occasionally be attributed in part to this cause. The mechanical condition of the oxides previous to blasting was not always the same, and it seems not improbable that this fact may be of some importance where intense blasting is resorted to in order to remove the last traces of oxygen necessary to effect a complete transition from an oxide which, for example, is stable at the temperature reached by the Bunsen burner to one of a lower state of oxidation which may be the stable form at the temperature produced by the more intense heat of the blast-lamp. Judging from the experience of Hitch-

[1] Chemie der seltenen Erden. p. 63.
[2] *Ibid.*, p. 122.

cock, and from the fact that blasting invariably reduced the weights, it seems probable that, in the case of some of the elements, at least, an oxide of a higher state of oxidation was more stable over the Bunsen burner than over the blast-lamp. Such behaviors have been noticed with some of the more common elements.

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FLUORIDE OF GOLD.[1]

BY VICTOR LENHER.

Received September 8, 1903.

INASMUCH as fluorspar is frequently associated with gold in nature, and quite notably so in the deposits of the telluride ores, it has seemed important to study gold fluoride in order to determine, if possible, whether this substance can play any part in the genesis of these deposits.

The known compounds of gold with the halogens chlorine, bromine and iodine, are, as a rule, fairly well defined. In the trivalent condition, gold forms the relatively stable chloride while the bromide and iodide show greater tendency to break down into the lower state of valence of gold.

The halides in which gold shows a monovalence have received considerable attention, and it is known with a reasonable degree of certainty under what conditions aurous chloride, bromide, and iodide are capable of existence.

While the chlorides, bromides and iodides of gold have received more or less study, comparatively little is known of fluoride of gold. Prat[2] has prepared an intermediate oxide of gold, Au_2O_2, by the incomplete solution of gold in aqua regia, in which the hydrochloric acid is in excess, treating the solution with sufficient potassium bicarbonate to dissolve the precipitate formed, and warming the clear orange-yellow solution to 95°, when a dark olive-green precipitate was obtained which, when dried, showed the composition Au_2O_2. In studying the properties of this oxide, Prat states that hydrofluoric acid combines with it but without dissolving it. In his study of the action of fluorine on the various metals, Moissan states that at a red heat, gold is attacked by

[1] Read before the Wisconsin Academy of Science, December 26, 1902, and published in the Transactions.

[2] *Compt. rend.*, **70**, 843.

fluorine gas, a yellow hydroscopic substance being formed, and that this substance is readily decomposed into gold and fluorine.

These two experiments give practically what is known of the fluoride of gold.

The activity of the halogens toward other elements is, as a rule, inversely proportional to their atomic weights. The first member of this group of active elements, fluorine, is certainly the most active of all the elements, be they halogens or not; yet, as will be demonstrated later, it appears to have little if any affinity for gold.

In studying the chemistry of gold, it should always be borne in mind that it is the most inactive of the metals, but the relative stability of the most of its salts, notably with the halogens, would appear to make probable the relative stability of the compound of the most active of the elements, fluorine. On the other hand, we have the marked difference of fluorine from the other halogens in the insoluble fluorides of calcium, strontium and barium, as contrasted with the very soluble chlorides, bromides and iodides; and the soluble fluorides of silver and thallium as compared with the insoluble chlorides, bromides and iodides.

In order to study the relations between fluorine and gold, experiments were conducted with the view of bringing about, if possible, the formation of gold fluoride under various possible conditions.

The first experiment made was a study of the action of hydrofluoric acid on gold oxide. To this end, gold oxide was prepared by the action of magnesium oxide on a solution of gold chloride and the excess of magnesia removed with nitric acid. The gold oxide thus obtained was finely divided, and hence in the most suitable condition to be susceptible to any chemical action. This gold oxide can remain in contact with hydrofluoric acid indefinitely or, as has been the case, can be boiled for weeks with either hydrofluoric acid alone or with a mixture of hydrofluoric and nitric acids, without suffering any change whatever. These experiments have been repeated several times, but in no case has gold been found to enter into solution, nor has it been possible to detect fluorine in the precipitate. It is obvious that gold fluoride cannot be prepared by the action of hydrofluoric acid on the oxide. The next most natural method to try

for the preparation of the fluoride would be that of double decomposition.

Silver fluoride and gold chloride, both being soluble salts, on being brought in contact in solution should yield theoretically:

$$AuCl_3 + 3AgF = AuF_3 + 3AgCl.$$

The actual case is that when solutions of these two salts are brought in contact, gold hydroxide is quantitatively thrown out of solution along with silver chloride; thus,

$$AuCl_3 + 3AgF + 3H_2O = 3AgCl + Au(OH)_3 + 3HF.$$

The accuracy of this reaction has been carefully established in the laboratory.

If gold fluoride is even momentarily formed, it is immediately decomposed by water.

The method yet remaining for the preparation of a substance incapable of existence in presence of water would be the use of anhydrous solvents. A large number of organic solvents have been tried with this end in view, but no substance has been found which would dissolve both gold chloride and silver fluoride; either these salts are insoluble or are decomposed by the substances worked with. Among the solvents examined, mention may be made of the following: Alcohol, ether, carbon bisulphide, benzene, turpentine, pentane, hexane, chloroform, carbon tetrachloride, ethyl nitrate, nitrobenzene, ethyl acetate, ethyl propionate, and pyridine.

It thus appears that gold fluoride is incapable of existence not only in presence of water, but under the ordinary conditions met with in the laboratory and in nature.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI, NO. 60.]

A METHOD FOR THE ESTIMATION OF CHLORIDES, BROMIDES AND IODIDES.

BY STANLEY BENEDICT AND J. F. SNELL.

Received September 3, 1903.

IN THE August number of this Journal we described a method for the detection of chlorides, bromides and iodides in presence of each other. The reagent used to liberate the iodine and bromine was potassium iodate, which sets free the iodine on acidifi-

cation with acetic and the bromine on acidification with dilute nitric acid. In the same paper we mentioned that the reaction with iodic acid had been employed by Bugarszky[1] for the quantitative separation of chlorides and bromides. He liberated the bromine with potassium biiodate and dilute sulphuric acid, and determined (1) the excess of biiodate and (2) the chlorine. This method is evidently inapplicable in presence of iodides. The purpose of the present paper is to describe a method of estimation of all three halogens when present together. It includes determinations of (1) total halogens, (2) iodine, and (3) chlorine, the bromine being estimated by difference.

The total halogens are determined by any of the ordinary methods, gravimetric or volumetric.

For the determination of the iodine, a suitable quantity of the substance (containing not over 0.5 gram iodine or 0.15 gram chlorine, if tenth-normal solutions are to be used) is dissolved in water and made up to about 50 cc. in a 100 cc. glass cylinder with close-fitting glass stopper. Neutral potassium iodate is added in about twice the quantity necessary to react with all the bromine and iodine believed to be present. The mixed solution is acidified with 4 or 5 cc. 5N (30 per cent.) acetic acid and shaken with 30-40 cc. carbon disulphide until all the liberated iodine has been taken up by the latter. The aqueous phase is now separated from the carbon disulphide phase by filtration through a wet filter, and the carbon disulphide is thoroughly washed with cold water on the filter. The filtrate and washings are reserved for the chlorine determination. The carbon disulphide solution is transferred to another beaker by puncturing the filter and is covered with 20-25 cc. 75 per cent. alcohol. Any carbon disulphide left adhering to the filter is rinsed down into the beaker with a portion of the 75 per cent. alcohol. The iodine is now titrated with sodium thiosulphate with constant stirring. No starch indicator is necessary.

For the determination of the chlorine, the aqueous filtrate from the carbon disulphide is treated with 5 cc. 5N nitric acid (sp. gr. 1.18) to liberate the bromine and is boiled in a covered beaker until colorless. The excess of iodate is next destroyed by adding a quantity of potassium iodide slightly in excess of the amount necessary to react with it. The solution is again boiled until colorless, 2 or 3 cc.

[1] *Ztschr. anorg. Chem.*, **10**, 387 (1895).

TABLE OF RESULTS.

	KI. Grams.	KBr. Gram.	NaCl. Gram.	KI. Grams.	KBr. Gram.	NaCl. Grams.	KI. Grams.	KBr. Gram.	NaCl. Gram.
Used	0.0798	0.0897	0.0893	0.0114	0.0640	0.0638	0.1140	0.1281	0.1277
Found	0.0796	(0.0896)	0.0896	0.0116	(0.0640)	0.0636	0.1138	(0.1285)	0.1275
Difference	−0.0002	....	+0.0003	+0.0002	....	−0.0002	−0.0002	....	−0.0002
" per cent.	−0.25	....	+0.34	+1.75	....	−0.31	−0.18	....	−0.16
Used	0.0456	0.0512	0.0510	0.1026	0.1152	0.1143	0.0228	0.2140	0.0255
Found	0.0457	(0.0511)	0.0510	0.1025	(0.1152)	0.1144	0.0230	(0.2141)	0.0252
Difference	+0.0001	....	0.0000	−0.0001	....	+0.0001	+0.0002	....	−0.0003
" per cent.	+0.22	....	0.00	−0.10	....	+0.09	+0.09	....	−0.12
Used	0.1710	0.0512	0.0127	0.0114	0.0128	0.0128	0.0114	0.0128	0.0127
Found	0.1704	(0.0507)	0.0128	0.0105	(0.0134)	0.0131	0.0116	(0.0125)	0.0128
Difference	−0.0006	....	+0.0001	−0.0009	....	+0.0003	+0.0002	....	+0.0001
" per cent.	−0.35	....	+0.79	−7.89	....	+2.34	+1.75	....	+0.80
Used	0.0057	0.0064	0.0635	0.1368	0.0064	0.0063	0.1228	0.3815	0.1518
Found	0.0060	(0.0062)	0.0634	0.1369	(0.0066)	0.0060	0.1225	(0.3816)	0.1520
Difference	+0.0003	....	−0.0001	+0.0001	....	−0.0003	−0.0003	....	+0.0002
" per cent.	+5.26	....	−0.16	+0.07	....	−4.76	−0.25	....	+0.13

more of the dilute nitric acid being added, if the color is not completely discharged after ten or fifteen minutes' boiling. A minute or two after the color has completely disappeared the solution is taken from the flame, cooled and neutralized with sodium carbonate. To secure exact neutralization, a little calcium carbonate may be added at first and then sodium carbonate solution until a precipitate just forms. The chlorine is then determined by titration with standard silver nitrate, using potassium chromate as indicator.

The results of twelve analyses of mixtures of potassium iodide, potassium bromide and sodium chloride are tabulated below. It will be observed that, with two exceptions, the differences between the taken and found quantities of potassium iodide and sodium chloride do not exceed 0.3 milligram.

ON CEROPTENE, A NEW ORGANIC COMPOUND.

By W. C. Blasdale.

Received August 21, 1903.

In an article published[1] in 1893 the writer briefly described an organic compound which had been obtained from the fronds of *Gymnogramme triangularis,* for which the name *ceroptene* was provisionally proposed. It was shown in that paper that this compound, together with others of unknown composition, was secreted by peculiar gland-tipped hairs, which were found in great abundance on the under surfaces of the fronds of the beforementioned plant. The yellow secretion is produced in such abundance as to completely envelop and conceal the dorsal surfaces of the fully developed fronds, whence the popular name of the plant, the "golden-back" fern.

Secretions of a somewhat similar character are produced by other species of ferns, especially certain groups of species belonging to the genera *Gymnogramme, Cheilanthes* and *Notholoena;* possibly, also the secretions produced by certain species of *Primula* are of a like nature. Though none of these secretions appear to have been submitted to a chemical investigation, the opinion expressed or implied in most of the botanical treatises, which deal with these plants is that they consist of wax. Goep-

[1] *Erythea* (botanical journal published at Berkeley from 1893 to 1899), 1, 252.

pert,[1] however, considered them to be of a resinous nature, though his only reason for doing so is their solubility in alcohol. Klotzsch[2] has also described a crystalline compound which he obtained accidentally by dissolving the indument from the fronds of various species of *Gymnogramme* with alcohol and allowing the solution to evaporate spontaneously. This substance melted at 50°, was soluble in hot water, and in the opinion of this investigator was a "pseudo-stearoptene," that is, a compound related to coumarine, an opinion for which very little evidence was offered.

Though the golden-back fern is a comparatively common species on the Pacific coast, the amount of secretion yielded by it is but small, and it has been a difficult matter to secure the large quantities necessary for the investigation. The work has been further hindered because many of the compounds obtained were of a tarry nature and could not be purified when working on the small amounts available. Inasmuch as a large number of facts regarding the properties of the compound ceroptene have been gradually acquired it has seemed advisable to publish these at the present time, even though final conclusions regarding its structural formula can not be offered.

PREPARATION OF CEROPTENE.

Experiments with a variety of solvents showed that the entire secretion is easily soluble in either benzene or petroleum-ether, more readily, however, in the former solvent. The dried fronds, exclusive of stems, were treated in an extraction apparatus with either one of these solvents till complete solution of the indument had been effected, the solution thus obtained filtered from spores, etc., the excess of solvent distilled off, and the residual solution allowed to evaporate. In time there appeared wart-like groups of platy crystals, together with a much larger amount of a yellow amorphous substance, the total yield ranging from 4.4 to 6.4 per cent. Repeated crystallization of the crystalline portion from either benzene, ethyl ether, or alcohol finally gave a compound which melted very sharply at 135°. This is the compound to which the name ceroptene has been given; it constitutes about one-third of the total secretion. The non-crystalline portion melts

[1] "*Actorum Academiæ Caesareæ Leopoldino-Carolinæ Naturæ Curiosorum*," **18**, Suppl. I, page 229.

[2] *J. prakt. Chem.*, **55**, 242.

at about 58° and is evidently a mixture of several substances, of which the only one identified with certainty is cerotic acid. Various methods of treating this portion were used; the most satisfactory was to digest with a dilute aqueous solution of potassium hydroxide, in which the cerotic acid is but slowly soluble, while the other constituents of the secretion dissolve almost immediately. The insoluble cerotic acid was purified by repeated treatment with hot alcohol. The alkaline solution was acidified, which reprecipitated the tarry substance held in solution, and the precipitate thus produced treated with a small amount of cold alcohol. This treatment left insoluble a further quantity of ceroptene and a very minute quantity of a second crystalline substance. Thus far but little progress has been made in the separation of the tarry products dissolved by the alcohol.

DESCRIPTION OF CEROPTENE.

The pure substance forms beautiful tabular or prismatic crystals of a sulphur-yellow color. It is readily dissolved by acetone, chloroform, carbon bisulphide, carbon tetrachloride, and less readily by ether. It is readily soluble in alcohol or benzene, but the solubility is greatly increased by a slight increase in the temperature of these solvents. Concentrated sulphuric, hydrochloric, or acetic acids readily dissolve ceroptene and it may be recovered from the two latter solvents by spontaneous evaporation. Dilution of all of the three acid solutions produces a light yellow precipitate, which on treatment with benzene yields the original ceroptene. With the sulphuric acid solution, however, the precipitation takes place very slowly and small amounts of tarry substances are produced at the same time. On heating, it fuses with the formation of a clear lemon-yellow liquid but, as the temperature is increased, decomposes with the formation of volatile compounds, which have a strong aromatic odor. By transmitted light, the crystals are of a clear lemon-yellow color, but by reflected light they show a pronounced green fluorescence. The alcoholic solution also shows the latter phenomena to a slight degree. Neither the crystals nor their solutions rotate the plane of polarized light. The specific gravity of the crystals at a temperature of 15°, compared with water at the same temperature, is 1.1976.

CRYSTALLOGRAPHY OF CEROPTENE.

Crystallization from different solvents produced individuals showing a considerable diversity of habit, though the number of distinct crystal forms concerned was not great. The best were obtained from benzene, from which solvent perfect individuals of flat, tabular form sometimes 2 cm. in length and 3 mm. in thickness could be obtained; chloroform or glacial acetic acid gave less perfect forms; alcohol usually gave needle-shaped or prismatic forms of smaller size. Examination of the crystals with polarized light in a direction at right angle to the plane of greatest development showed the emergence of an optic axis, the latter placed very eccentrically. This fact, as well as the symmetry of the crystal form, clearly classes them as triclinic. The plane of greatest development was, therefore, chosen as the base and the two planes showing the least inclination to it, as brachy- and macropinacoids; it was then easy to refer the remaining planes to either dome or prismatic faces. Although the crystals were well formed, many of the faces, especially the macropinacoid, failed to give good reflections owing to the curvatures or other imperfections. The accompanying table gives the results of the measurements of the principal interfacial angles.

MEASUREMENTS IN THE BRACHY ZONE.

Angle (001) $\wedge$ (010). Average of seven measurements, 67° 29′.

Angle ($0\bar{1}0$) $\wedge$ ($0\bar{1}1$). Average of two measurements, 55° 59′.

Angle (001) $\wedge$ ($0\bar{1}1$). Average of three measurements, 56° 57′.

Angle (001) $\wedge$ (011). Result of one measurement, 33° 39′.

MEASUREMENTS IN THE MACRO ZONE.

Angle (001) $\wedge$ (100). Average of four measurements, 85° 45′.

Angle ($\bar{1}00$) $\wedge$ ($\bar{1}01$). Average of two measurements, 42° 52′.

Angle (001) $\wedge$ ($\bar{1}01$). Average of eight measurements, 50° 49′.

MEASUREMENTS IN THE VERTICAL ZONE.

Angle (100) $\wedge$ (010). Average of five measurements, 84° 11′.

Angle ($0\bar{1}0$) $\wedge$ ($1\bar{2}0$). Average of five measurements, 30° 24′.

Angle (100) $\wedge$ ($1\bar{2}0$). Average of three measurements, 66° 10′.

From the figures representing the inclinations of the three pinacoids, the following values were calculated[1] for the inclinations of the axes:

[1] The writer desires to acknowledge his indebtedness to Dr. A. S. Eakle, of the Department of Mineralogy, for assistance in making the calculations.

$$\alpha = 112° 13', \beta = 92° 12', \gamma = 94° 33'.$$

From the inclinations of the two dome faces (d and e of the figures) on the base, the following values for the axial ratios were obtained:

$$a = 0.8353, b = 1, c = 1.0138.$$

From the intersection of the face m on the brachy- and macropinacoids, the intersection of that plane on the a and b axes respectively, was found to be 1.757; 1, hence its formula is (120). It was observed only when truncating the more acute of the two prismatic angles formed by the intersection of the macro- and brachy-diagonal sections. The macrodome face was present only when of the form $(10\bar{1})$. The brachydome face of the form $(0\bar{1}1)$ was the one usually present, though the form (011) was observed in two instances. Some of the more common combinations are shown in the accompanying figures in which $a = (100)$, $b = (010)$, $c = (001)$, $d = (0\bar{1}1)$, $e = (10\bar{1})$, $f = (011)$, $m = (\bar{1}20)$.

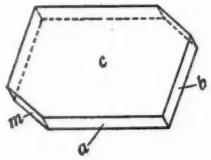

Fig. 1.

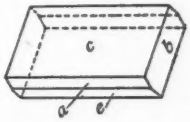

Fig. 2.

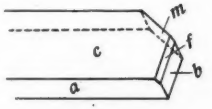

Fig. 3.

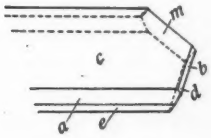

Fig. 4.

FORMULA OF CEROPTENE.

In order to obtain satisfactory material for the quantitative examination, very careful preparation was found to be necessary, since the crystals tend to retain very tenaciously small amounts of the waxy constituents of the secretion. Failure to discover this fact led to an erroneous determination of the formula in the

first work on the subject. Of the results recorded below, No. 1 represents materials recrystallized three times from ether, after the preliminary purification, Nos. 2 and 3 were obtained similarly by three recrystallizations from benzene and Nos. 4 and 5 by three recrystallizations from absolute alcohol.

	(1)	(2)	(3)	(4)	(5)	Average.
Carbon.....	72.26	72.42	72.62	72.62	72.51	72.48
Hydrogen.....	6.37	6.16	6.13	6.16	6.20	6.20

These figures indicate that the formula of the compound is $(C_9H_9O_2)_n$, the theory for which is C = 72.44, H = 6.09.

The molecular weight was determined by the freezing-point method, using the usual form of Beckmann apparatus. The results obtained were: With benzene as a solvent, 253, 264, 255; with glacial acetic acid as a solvent, 268, 280; with phenol as a solvent, 259.

The correct formula of the compound then must be $C_{18}H_{18}O_4$ (molecular weight = 298), the low results obtained being probably due to a slight amount of dissociation.

REACTIONS OF CEROPTENE.

The compound possesses decided acid properties. It is dissolved readily by even dilute solutions of the alkaline hydroxides, and these solutions remove it rapidly from a benzene solution of the compound. Long-continued treatment with hot solutions of sodium or barium carbonate or borax dissolve it to some extent. In spite of these facts, it is a difficult matter to prepare the pure salts, owing to their unstability.

If a solution of ceroptene in an alkaline hydroxide is gradually concentrated, oily, yellowish-brown drops finally appear in the bottom of the vessel; these solidify, on cooling, with the formation of a hard, yellow mass, which is easily soluble in water. If some of this solid yellow mass is dissolved and the solution thus obtained is allowed to evaporate spontaneously, the ceroptene gradually separates out in the form of granular masses and the residual solution becomes alkaline. Dilution of alkaline solutions of ceroptene does not bring about precipitation, but neutralization results in the formation of a light yellow precipitate, and, when this is dissolved in benzene, ceroptene crystals of the usual form are produced on evaporation. All

the alkaline solutions possess a much more intense color than solutions of the corresponding concentration in organic solvents. Two samples of the potassium salt, prepared with the use of the smallest possible excess of the alkali and separated as solid yellow masses, gave 11.94 and 11.42 per cent. of potassium, respectively. A salt corresponding to the composition $C_{18}H_{17}KO_4$ should contain 11.64 per cent.

The barium salt was prepared by boiling ceroptene with a slight excess of barium hydroxide, filtering the hot solution into a flask previously filled with hydrogen, and allowing to stand. After several days, there appeared a beautifully crystalline salt of a deep yellow color. It is but slightly soluble in water and, on heating, decomposes before reaching a definite melting-point. Determination of the per cent. of barium in two preparations of the salt gave 17.92 and 17.79 per cent., respectively. These figures would indicate a compound corresponding to the formula $(C_{18}H_{17}O_4)_2Ba.2H_2O$, which should contain 17.87 per cent. of barium and 4.69 per cent. of water of crystallization. Experiments in heating the salt showed no appreciable loss up to a temperature of 120°, but at 160° the salt lost 5.23 per cent. in weight and there was some evidence of decomposition.

The silver and lead salts may be obtained by the addition of the nitrates of these metals to solutions of the potassium salt. As thus obtained, they consist of gray, amorphous precipitates which are difficultly soluble. Determination of the silver in a sample of this salt (probably contaminated with small amounts of silver oxide) gave 27.62 per cent. of silver, whereas the anhydrous salt should contain 26.66 per cent.

Attempts to acetylize ceroptene, using glacial acetic acid as a solvent and various combinations of acetic anhydride, acetyl chloride and sodium acetate were entirely unsuccessful. Either the original compound was obtained unchanged, or tarry decomposition products only were produced. Similarly, treatment with benzoyl chloride failed to give any evidence of a definite reaction. With bromine in a chloroform solution, ceroptene liberates at once hydrobromic acid, but the other products of the reaction are non-crystalline and could not be purified. With "Hübl's mixture," using the usual method for the determination of the iodine absorption, no absorption of iodine was shown.

Phenylhydrazine and hydroxylamine do not react with ceroptene under the conditions which usually bring about reactions with aldehydes or ketones, and no bisulphite compound could be prepared. No indications of reducing properties could be obtained by the use of the usual reagents, *i. e.*, alcoholic silver nitrate, Fehling's solution, etc.

Oxidizing agents, dilute nitric acid or potassium permanganate or bichromate in alkaline solution, added to ceroptene and heated, at once give a pronounced odor of benzaldehyde. When 0.5 gram of ceroptene was heated with potassium permanganate for an hour, filtered from the precipitate of manganese dioxide which is formed, acidified and extracted with ether, a white crystalline compound was obtained. This, after purification by recrystallization, was found to melt at 122°, and was sublimed without change. When it was dissolved in absolute alcohol, the solution saturated with dry hydrochloric acid gas, and the whole poured into cold water, oily drops having the characteristic odor of ethyl benzoate separated out. Some carbon dioxide is produced during the oxidation, but it is evident that the chief product of the reaction is benzoic acid, though it is probable that the corresponding aldehyde is first produced.

The treatment of a glacial acetic acid solution of ceroptene with concentrated aqueous hydriodic acid at a temperature of 60° or above, produces a crystalline iodo-compound, which melts at 182°. This appears in crystalline form on cooling the hot mixture, and continues to separate from the solution during several days. The yield obtained in six different preparations ranged from 131 to 145 per cent. of the ceroptene used. Many attempts were made to separate other products of the reaction from the acid mixture, but in every case only tarry compounds, which in solubility, etc., seemed to be identical with the crystalline iodo-compound, were obtained. Iodine is not liberated during the reaction, nor was any considerable amount of the free iodine, which was present in the hydriodic acid used, taken up. The reaction does not take place when other solvents are substituted for the acetic acid, nor does an analogous reaction take place when hydrochloric or hydrobromic acids are used in place of hydriodic acid.

THE IODO-COMPOUND.

The crystals are needle-shaped, often an inch long, with blunt terminations, but the faces are too imperfect to admit of crystallographic study. By transmitted light they are red-brown, but by reflected light they are dark purple. On heating, they first melt with the liberation of iodine, then carbonize, and finally burn without residue. They are insoluble in water, carbon bisulphide and petroleum ether, only slightly soluble in glacial acetic acid, benzene and nitrobenzene, but readily so in alcohol and acetone. It is, however, almost impossible to recrystallize the compound from any of these solvents; when dissolved in alcohol or acetone, the solution leaves, on evaporation, a black, tarry mass which seems to possess all the chemical properties of the original crystals. If acetic acid is added to the acetone solution, a very small amount of the compound separates in crystalline form, the remainder as an amorphous mass. The composition of the compound is shown in the following analyses, each of which represents a different preparation, obtained by washing the crystals, which separated out with glacial acetic acid, and drying at 110°. The iodine was determined by the Carius method, but most of the determinations are somewhat high, owing to the presence of minute particles of glass which could not be separated from the precipitate.

	(1)	(2)	(3)	(4)	(5)	Average.
Carbon	41.26	41.20	41.34	41.07	41.22	41.22
Hydrogen	....	3.44	3.43	3.44	3.41	3.43
Iodine	....	40.25	40.84	40.69	....	40.59

These figures correspond most nearly to the composition $C_{11}H_{11}IO_3$, the theory for which is C = 41.51, H = 3.46, I = 39.94.

The molecular weight was determined with approximate accuracy only; the small amount of material available necessitated the use of freezing-point methods and the very slight solubility, in the solvents commonly employed, introduced a large percentage error in these determinations. Using nitrobenzene as a solvent, two approximate results, 310 and 357 respectively, were obtained. The theory for $C_{11}H_{11}IO_3$ is 318. These results are sufficient to establish the formula of the compound as written above.

REACTIONS OF THE IODO-COMPOUND.

The iodo-compound shows acid properties similar to those of ceroptene, but the preparation of the pure salts is attended with many difficulties. The salts are characterized by red or brown colors and possess weak dyeing properties with woolen goods. An approximately pure potassium salt yielded 15.27 per cent. of potassium; the compound $C_{11}H_{11}KO_4$ should contain 15.89 per cent. If an alkaline solution of the iodo-compound is acidified, there is produced a yellow precipitate which coagulates to form resinous masses. It is soluble in alcohol, acetone, chloroform and glacial acetic acid, but it can not be crystallized from any of these solvents or combinations of them. It does not contain iodine and melts very indefinitely at 52°. Owing to its amorphous nature and the difficulty of drying without effecting decomposition, an accurate determination of its formula could not be made. The result of three combustions and a single molecular weight determination indicate that the formula is $C_{11}H_{12}O_4$.

On oxidizing the iodo-compound with nitric acid or potassium permanganate, as in the treatment of ceroptene, similar evidence for the formation of benzaldehyde and benzoic and carbonic acids was obtained. With the usual reagents for the detection of aldehyde or ketone groups, no evidence of any reaction could be obtained. Attempts to reduce with sodium amalgam and also with metallic magnesium led to the formation of compounds which could not be purified.

The exact nature of the reaction involved in the formation of the iodo-compound is still a mystery. Apparently, it is the only product of that reaction. If it be assumed that 1 molecule of ceroptene produces 1 molecule of the iodo-compound, the theoretical yield should be 106.7 per cent. Since the actual yield varies from 131 to 145 per cent. and since a large amount of a non-crystalline compound, which seems to be identical with the crystalline product, is produced at the same time, it is probable that 2 molecules of the iodo-compound are produced from 1 of ceroptene. Evidently the acetic acid takes part in the reaction, as is also evinced by the failure to obtain the compound when other solvents are used. Further, this involves more than the simple addition of an acetyl group, since no evidence of acetic

acid nor of any volatile compound could be obtained on saponifying, acidifying the product, and distilling. As to the structure of the iodo-compound, it can only be said at present that it contains a single benzene nucleus with a side chain, and that, since the iodine is easily displaced, it is not a part of a second ring, though as the substance does not add iodine, and hence contains no ethylene groupings, it is somewhat difficult to write a structural formula in which the ring structure is absent. At first sight it would seem as though the quantitative relation involved in the formation of the iodo-compound would indicate that ceroptene was composed of two symmetrical groups, each containing a single benzene nucleus, which is split by the hydriodic acid. If this were strictly so, however, the formation of dibasic as well as monobasic salts should be expected. Any attempt to express the probable structure of either compound is at present unprofitable.

IDENTIFICATION OF CEROTIC ACID.

If the waxy portion of the secretion, which remains after the separation of the ceroptene, is digested with hot alcohol, filtered while hot, and allowed to cool, a white amorphous precipitate separates out. This precipitate fused at 64° and, on cooling, formed a hard, brittle mass. By two further precipitations from alcohol, a product was obtained which melted at 70°. A more rapid method of separating the same substance was to digest the wax with a dilute solution of an alkaline hydroxide and treat the undissolved portion with alcohol as in the other method. When obtained by either process, the product was of a greenish color after fusion, was readily soluble in petroleum ether, acetone and ethyl ether, and was precipitated from the solution by lead acetate. The alcoholic solution shows only faint acid properties, and the amount of potassium hydroxide necessary to react with 1 gram, determined by the ordinary process for saponification number, was found to be 0.22 gram. The combustion of three different preparations gave the following results:

	(1)	(2)	(3)	Theory for $C_{27}H_{24}O_2$.
Carbon	79.04	78.29	80.24	78.94
Hydrogen	12.32	12.56	13.30	13.26

A single determination of the molecular weight by the freezing-point method, using benzene as the solvent, gave 482, though the percentage error involved in this determination is comparatively

large, owing to the very slight solubility in this solvent. In all the particulars noted above, the substance agrees so closely with the substance originally separated by Brodie from beeswax that there can be little doubt that it is essentially cerotic acid. The preparations thus far obtained are impure.

THE OTHER CONSTITUENTS OF THE SECRETION.

As noted earlier in this paper, a second crystalline compound is obtained from the tarry precipitate produced by acidifying the alkaline solution of the secretion. Treatment of this precipitate with alcohol leaves a small amount of ceroptene, together with the substance just referred to. It is a difficult matter to separate it from the ceroptene, but a long series of fractional crystallizations from acetone finally separated it in pure condition. It forms brown, monoclinic prisms which melt at 185°. Some of these were obtained large enough for crystallographic study. The only forms present were the prism, basal plane and clinopinacoid. The angles measured were as follows:

$(110) > (1\bar{1}0)$ (average of 9 measurements) $= 77° 32'$
$(110) > (001)$ " " 4 " $= 57° 31'$
$(010) > (001)$ (result of a single measurement) $= 89° 34'$.

Barely enough of the pure substance was obtained for a single combustion, the results of which were C = 69.01 per cent., H = 4.95 per cent.

That portion of the acid precipitate which is easily soluble in cold alcohol, and which forms nearly one-half the total secretion, is of an entirely amorphous nature. In a long series of experiments with a great variety of solvents, only brown, sticky compounds were obtained. The compounds of which this material is composed are evidently strongly acid in character, and their lead salts are insoluble. Combustions of several samples of the substance gave results varying from 57.76 to 68.33 per cent. of carbon, and from 7 to 7.17 per cent. of hydrogen. The material is clearly a mixture of several acids.

CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA, August 15, 1903.

THE HYDROCARBONS IN LOUISIANA PETROLEUM.

By Charles E. Coates and Alfred Best.

Received September 1, 1903.

The excitement which followed the discovery of the Beaumont oil field in Texas and the speculation which attended its development, have, to some extent, drawn the attention of the public from the development of the petroleum fields of Louisiana. Of these, the fields at Welsh and at Jennings have already passed into a solidly commercial condition, while at Anse la Butte, and at numerous other points in Southern Louisiana, oil has been found in considerable quantity. It is the intention of the writer to publish later an account of the chemical nature of the various oil pools in Louisiana. In view of the fact, however, that very little information is available in regard to this matter, it has been considered advisable to present here the results of some work done in this laboratory during the past six months. Early in the spring, samples of oil were secured from Beaumont, Texas, and from the oil fields near Welsh, Jennings, and Breaux Bridge in Louisiana. These oils were distilled from Engler flasks with the usual precautions. Their fuel values were determined with a Parr calorimeter, which gave concordant results on duplicate determinations and proved in every way satisfactory.

In the distillations, it was found that the time taken influenced the results to such an extent that no measurements were concordant above 300°. This is, doubtless, due to the decomposition of the higher fractions, these breaking down slowly into fractions both of lower boiling-point and of higher boiling-point than the original fraction.

The following table shows the results of these examinations:

In the table the distillations were made in duplicate and agreed fairly well. The relative evolution of hydrogen sulphide, at low temperatures, is worth consideration, both from the standpoint of pumping the crude oil and of refining it. The figures obtained for the Beaumont oil differ somewhat from those previously published. It would seem that it had gotten heavier than it was when the Lucas well was first opened, and it also shows a general rise in the boiling-points of the fractions. There are now no gushing wells at Beaumont, and many which once pro-

	Texas. Beaumont.	La. Welsh.	La. Jennings.	La. Breaux Bridge.
Specific gravity 25° C.	0.9228	0.9276	0.9093	0.9392
Distillation begins	150° C.	230° C.	200° C.	240° C.
Distillation, Engler flasks, 760 mm.	per cent.	per cent.	per cent.	per cent.
To 150° C.	none	none	none	none
150°–200°	2	none	none	none
200°–250°	8	2	13	1
250°–300°	26	17	28	15
300°–350°	26	23	24	22
350°–to asphalt	30	49	30	53
Asphalt residue	8	9	5	9
H_2S evolved on heating	in large quantities 115°–150°	in very small amount at 230°	in small quantity 200°	in very small amount at 240°
Color of lower fractions	yellow	nearly colorless, light yellow on standing	colorless, yellowish on standing	slightly yellow
Fuel value in B. T. U.	19923	19000	19814	19300
Illuminating oil fractions to 300°	36	19	41	16
Estimated depth of well	1200	700 (?)	1000	600
Per cent. sulphur in crude oil	1.96	0.32	0.39	0.20

duced oil on pumping, have been abandoned. The field at Jennings is of greater area, and less initial pressure. The proved field there is growing and the wells, while not phenomenal, are considered profitable. There is, as yet, no reason to fear that the field is losing in producing power. This is also true of the Welsh field. The geology of these oil deposits is still somewhat obscure. It has been suggested that they are pools, gathered under pressure in the top of a dome with sharply descending sides. Such a deposit would possibly be larger when the angle of the dome was more obtuse. There are, throughout Southern Louisiana, certain elevations of an otherwise flat country. They are generally of limited area and rise only a very few feet above the surrounding plain. These elevations are considered superficial indications of gas pressure beneath and, consequently, of oil. There is also a certain amount of seepage, and some springs show oil in their water. None of these indications are reliable as establishing the existence of an oil pool, which fact, however, would seem to make it probable that many such pools may still remain undiscovered.

In the following investigation the sample sent from Breaux Bridge was taken, first, because it was sent in considerable quantity. The methods employed were those suggested by Mabery in his recent investigations of the Texas oils, and by Richardson and Wallace in their paper on the Beaumont field. A similar treatment of Jennings and Welsh fields will follow as soon as time permits.

The oil in question was sent by the Moresi Co., of Jeanerette, La. It was taken from a 600-foot stratum at Anse la Butte, near Breaux Bridge, La. This is considered a shallow well. There are others at Anse la Butte which are 1000 feet deep and produce 15 to 30 barrels daily. The crude oil was low in sulphur, an analysis, by the Carius method, showing only 0.2 per cent. It was black, viscous and had a not unpleasant odor, somewhat resembling turpentine. The specific gravity, at 25°, was 0.9392. Distilled in an Engler flask, at atmospheric pressure, it gave no gasoline and 16 per cent. illuminating oil—the fractions up to 300° C. Heated to 350° C., 22 per cent. more oil was obtained. Heated above this to asphalt, the distillate was a dark, heavy, fluorescent oil with a somewhat unpleasant odor. After the

limit of the thermometer employed, 400°, was reached, it was removed and distillation continued until little more oil came over. The residue, amounting to about 9 per cent., was heated in an open dish until it was about one-fourth evaporated. The resulting mass was asphaltic in its nature, being hard, black and shiny, with a conchoidal fracture. It had a specific gravity of 1.123. On burning in a closed platinum crucible, as in coal analysis, the following results were obtained:

Volatile matter	71.0
Fixed carbon	28.6
Ash	0.4

Compared roughly with paving asphalt, the physical qualities of this residue appeared only fair.

An attempt was made to refine the illuminating oil fraction by sulphuric acid, in the usual way, washing with sodium hydroxide. It was found practically impossible to secure a water-white product. The most nearly colorless products obtained turned yellow in a few days, on standing in an open Erlenmeyer flask. About 15 per cent. of sulphuric acid was used, and there was a loss of about 12 per cent. of oil, though these figures could probably be reduced in practice. The refined oil was tested in an ordinary flat-wick lamp. It burned freely with a somewhat smoky yellow flame and a pleasant resin-like, aromatic odor, differing altogether from that of ordinary kerosene. Upon replacing the lamp chimney with one considerably taller, the yellow flame became white and no longer smoked. As the oil was almost free from sulphur, the fraction, up to 300°, was burned without refining at all and seemed to do as well as the refined oil. Still, considering the limited quantity of illuminating oil present, its poor quality and the small amount of asphalt, it would seem that, in the present state of chemical technology, the Breaux Bridge oil is fitted mainly for fuel purposes. For these it is well adapted, containing but little sulphur and being slightly higher in fuel value than the California petroleums, which are now used for fuel in large quantities. Its lubricating qualities have not, as yet, been tested, though it is said to have been used locally with good results.

In order to obtain fractions suitable for combustion, 500 cc. portions were distilled from a liter distilling flask, with the following results:

	Per cent.
Below 220° C.—atmospheric pressure	none
220°–240° C.—atmospheric pressure	0.3
240°–260° C.—atmospheric pressure	2.
260°–280° C.—atmospheric pressure	8.
280°–300° C.—atmospheric pressure	6.
300°–320° C.—atmospheric pressure	5.
160°–200° C.—at 60 mm. pressure	5.
200°–245° C.—at 60 mm. pressure	11.
245°–285° C.—at 60 mm. pressure	20.
285°–320° C.—at 60 mm. pressure	6.

This was repeated several times until a considerable quantity collected at certain points. The corresponding fractions were then mixed and the series subjected to fractional distillation at 60 mm. It was found exceedingly difficult to obtain a fraction with a constant boiling-point. Portions which came over at, say 165°-167°, would, on redistillation, break up into a series of products, ranging from 150°-180°, the portion remaining in the flask always being darkened and showing some decomposition After considerable trouble, three fractions were obtained, boiling at 110°-115°, 160°-165°, and 210°-215°, respectively. These were shaken with fuming sulphuric acid, washed with water, sodium hydroxide, and water again, then dried over calcium chloride, and redistilled. In order to prevent decomposition of the higher hydrocarbons, the 210°-215° fraction was dissolved in gasoline before adding the sulphuric acid, and the gasoline subsequently distilled off, as recommended by Mabery and Buck.[1] Each fraction lost considerably on the acid treatment, but the amount was not measured, since so much sulphuric acid was used as to preclude its use, practically, in refining.

The 110°-115° (60 mm.) fraction boiled at 205°-210° at 760 mm., with slight decomposition; it was water-white, and had an odor so strongly resembling turpentine that it was difficult to distinguish them, one from the other. This odor was not affected by the acid treatment. A portion of the oil was polarized, but showed no optical activity. This odor is so marked that a similar distillate, obtained in the Jennings refinery, is now being offered for sale as a turpentine substitute, and the makers claim it answers its purpose well. The specific gravity of the 110°-115° fraction was 0.8479 at 27°. Its molecular weight was determined by the

[1] This Journal, **22**, 555.

freezing-point method, benzene being used as a solvent; 161 was found; calculated for $C_{12}H_{22}$, 166. A combustion of the oil gave, for carbon, 86.4 per cent., and for hydrogen, 13.38; calculated for $C_{12}H_{22}$, carbon, 86.74 per cent.; hydrogen, 13.26.

The 160°-165° fraction (60 mm.) was treated in the same way as the preceding one. It had none of the turpentine-like odor. Its specific gravity at 29° was 0.8785. Its molecuar weight, by the freezing-point method, with benzene, was 189; calculated for $C_{14}H_{26}$, 194. On combustion it gave, for carbon, 86.79 per cent., and for hydrogen, 13.1. Calculated for $C_{14}H_{26}$, carbon, 86.59 per cent.; hydrogen, 13.41.

The 210°-215° fraction (60 mm.) was treated as was the preceding. Its specific gravity at 29° was 0.9009. Its molecular weight, by the freezing-point method, was 233; calculated for $C_{17}H_{30}$, 234. Upon combustion it gave, for carbon, 87.15 per cent., and for hydrogen, 12.72 per cent. Calculated for $C_{17}H_{30}$, carbon, 87.18 per cent.; hydrogen, 12.82 per cent.

From the above figures it is evident that the series C_nH_{2n-2} and C_nH_{2n-4} are the main constituents of this oil. This corresponds with the conclusions reached by Mabery and Buck[1] on some Texas oil, and also by Mabery[2] on the Beaumont oil. Mabery considers the series C_nH_{2n-2} as belonging to the dicyclic polymethylene series, in which view Richardson and Wallace concur. By analogy, the series C_nH_{n-4} might be looked upon as being desired from dihexahydrofluoren, C_6H_{10}—C_6H_{10}; but there

is, as yet, little positive evidence as to the structure of either series. They are almost certainly not unsaturated aliphatic compounds, however, for they do not behave as though unsaturated. If they are cyclic compounds, they might respond to Nikiforoff's methods of consecutive decomposition under increased pressure, which has succeeded in producing benzene derivatives of excellent quality from Russian petroleum. That Louisiana petroleum does undergo progressive decomposition, under continued distillation, has been established in the course of this investigation.

[1] *Loc. cit.*

[2] This Journal, 1901, p. 264.

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BATON ROUGE.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 90.]

ON THE INFLUENCE OF DIET, MUSCULAR EXERTION AND LOSS OF SLEEP UPON THE FORMATION OF URIC ACID IN MAN.

BY H. C. SHERMAN.

Received September 11, 1903.

WITHIN the last few years much attention has been given to the behavior of the nucleins and purin bodies in the human organism, and the sources and significance of the uric acid eliminated. This work has been so fully discussed by recent writers,[1] that it is unnecessary to review it here. The principal workers are agreed that the uric acid eliminated comes, in part, from the activities within the body and, in part, from the purin bodies ingested, either as such or as constituents of the nucleins, the former being sometimes called the "endogenous," the latter the "exogenous" uric acid. No general agreement exists, however, in regard to the causes or limits of variation in either the endogenous or the exogenous portion. The daily elimination of uric acid by healthy men, on diets believed to be practically free from purin bodies, has been variously reported at from 0.20 to 0.60 gram. Burian and Schur hold that this variation in the endogenous uric acid is a matter of individual peculiarity, but that the exogenous portion bears quantitative relations to the different purin compounds of the ingested foods. Other investigators have failed to confirm the latter claim and hold that this exogenous portion is also influenced by other causes. Evidently these questions can only be settled by the accumulation of data regarding the influence of various conditions upon the elimination of uric acid by different healthy men.

Some years ago, in connection with a study belonging to the nutrition investigations of the United States Department of Agriculture,[2] the writer had opportunity to determine the uric acid eliminated by professional bicycle riders during a six-day race, involving such severe and long-continued exertion as would only be possible for well-trained athletes of unusual strength and en-

[1] Burian and Schur: *Archiv. für ges. Physiol.* (Pflüger), **80**, 241; **87**, 239; **94**, 273. Loewi: *Archiv. experimen. Path. and Pharm.*, **44**, 1; **45**, 157. Weiner's "Ergebnisse der Physiologie," 1902.

[2] U. S. Dept. of Agr., Office of Experiment Stations, Bull. 98. "The Effect of Severe and Prolonged Muscular Work upon Food Consumption, Digestion and Metabolism," by W. O. Atwater and H. C. Sherman.

durance. The subjects rode usually about twenty hours per day, sleeping only one or two hours in every twenty-four, and the food consumed was large in amount and, in some cases, contained large quantities of meat extract. As there was no opportunity to experiment with these subjects, except during the race, it was impossible to judge in how far the results of muscular exertion were complicated by those of diet and loss of sleep, and the figures for uric acid were, therefore, not published. Since that time it has been possible to experiment with another subject regarding the influence of loss of sleep, as well as with some of the foods used by the racers, and it is believed that the results can now be interpreted with sufficient accuracy to render them of value.

OBSERVATIONS UPON PROFESSIONAL BICYCLE RACERS.

A detailed description of the subjects and their work, diet and metabolism will be found in the bulletin cited above. The principal data bearing upon the present discussion, may be summarized as shown on pages 1161 and 1162.

It will be noted that large amounts of food were consumed and large quantities of nitrogen eliminated. The elimination of uric acid was not, as a rule, increased in proportion to the total nitrogen, but was in most cases somewhat and in some cases considerably above the normal. Before considering whether this increase of uric acid should be attributed to the diet or the work, the possible influence of loss of sleep may be noted.

INFLUENCE OF LOSS OF SLEEP.

In connection with certain experiments with another subject, "S," the details of which are described elsewhere,[1] the uric acid elimination was observed for a period of several days, the diet being kept constant and all the conditions as nearly uniform as possible, except that during three consecutive days the amount of sleep was materially reduced. The food of each day consisted of 300 grams bread (soda-crackers), 2,040 grams milk, and 40 grams butter. The principal results are given on page 1163.

[1] U. S. Dept. of Agr., Office of Experiment Stations, Bull. 121. "Experiments upon the Metabolism of Nitrogen, Sulphur and Phosphorus in the Human Organism."

Subject.	Day of race.	Sleep (about). Hrs. and min.	Distance ridden. Miles.	Food consumed.	Nitrogen in urine. Grams.	Uric acid in urine. Grams [2]
"M"	1[1]	0:0	441.8	Eggs, 43 grams; milk and kumyss, 7828 grams; boiled rice, 360 grams; sugar, 72 grams; fruit, 480 grams.	35.1	1.00
	2	1:40	366.7	Meat extract, 127 grams; eggs, 173 grams; milk and kumyss, 3261 grams; boiled cereals, 643 grams; sugar, 92 grams; fruit, 999 grams.	42.7	1.07
	3	1:35	334.1	Meat extract, 311 grams; milk, 4937 grams; bread, 35 grams; boiled cereals, 877 grams; pastry, 142 grams; sugar, 53 grams; fruit, 2003 grams.	46.2	1.50
	4	1:10	316.5	Meat extract, 43 grams; milk and matzoon, 1057 grams; rice pudding, 737 grams; pastry, 71 grams; fruit, 1459 grams.	35.7	1.71
	5	1:5	327.8	Meat extract, 9 grams; eggs, 94 grams; milk, 823 grams; soup, 113 grams; boiled cereals, 386 grams; sugar, 25 grams; pastry, 1009 grams; fruit, 870 grams.	30.7	1.15
	6	2:30	220.5	Meat extract, 5 grams; milk, 1985 grams; boiled rice, 422 grams; pastry, 1189 grams; sugar, 19 grams; fruit, 2161 grams.	26.9	1.00
"P"	1[1]	?	863.2	Eggs, 79 grams; milk and kumyss, 6122 grams; boiled cereals, 1080 grams; sugar, 89 grams; fruit, 19 grams.	32.8	0.62
	2	?		Meat extract, 85 grams; eggs, 46 grams; milk and kumyss, 4729 grams; boiled cereals, 887 grams; sugar, 85 grams; fruit, 255 grams.	43.6	0.84
	3	?		Meat extract, 156 grams; butter, 28 grams; milk and kumyss, 4340 grams; bread, 307 grams; boiled cereals, 1118 grams; sugar, 80 grams; fruit, 235 grams.	40.3	1.06
"A"	1	0:0	402.0	Meat, 85 grams; beef tea, 440 grams; eggs, 241 grams; milk, 531 grams; malted milk, 91 grams; jelly, 42 grams; bread, 459 grams; boiled cereals, 935 grams; sugar, about 200 grams; fruit, 434 grams.	25.3	0.88

[1] Subjects "M" and "P" dined heartily upon beefsteak about two hours before the beginning of the race.
[2] Determined by the Ludwig-Salkowski method.

Subject.	Day of race.	Sleep (about). Hrs. and min.	Distance ridden. Miles.	Food consumed.	Nitrogen in urine. Grams.	Uric acid in urine. Grams.
"A"	2	1 : 30	371.3	Meat, 148 grams; broth, 170 grams; beef juice, 128 grams; butter, 64 grams; eggs, 57 grams; milk, 116 grams; malted milk, 82 grams; jelly, 99 grams; bread, 204 grams; boiled cereals, 347 grams; sugar, about 250 grams; fruit, 1195 grams.	32.8	0.90
	3	0 : 20	352.7	Meat, 149 grams; meat extract, 24 grams; broth, 283 grams; eggs, 369 grams; butter, 78 grams; milk, 142 grams; malted milk, 78 grams; jelly, 213 grams; soup, 191 grams; bread, 361 grams; boiled cereal, 532 grams; sugar about 400 grams; fruit, 933 grams; cocoa wine, 170 grams.	39.0	1.08
	4	2 : 0	285.3	Meat, 206 grams; meat extract, 43 grams; broth, 879 grams; eggs, 283 grams; butter, 198 grams; milk, 312 grams; malted milk, 36 grams; jelly, 269 grams; bread, 659 grams; sugar, about 300 grams; fruit, 928 grams; cocoa wine, 198 grams.	65.1	2.50
	5	3 : 40	229.4	Meat, 326 grams; broth, 305 grams; eggs, 56 grams; butter, 220 grams; milk, 149 grams; malted milk, 21 grams; jelly, 156 grams; bread, 709 grams; tapioca pudding, 170 grams; sugar, about 300 grams; fruit, 1495 grams; cocoa wine, 43 grams.		
	6	2 : 0	181.9	Meat, 220 grams; broth, 701 grams; eggs, 114 grams; butter, 92 grams; milk, 269 grams; malted milk, 7 grams; jelly, 220 grams; bread, 496 grams; tapioca pudding, 142 grams; sugar, about 330 grams; fruit, 673 grams; cocoa wine, 113 grams.	39.8	1.63

Days.	Sleep (about). Hours.	Amount of urine. Grams.	Nitrogen in urine. Grams.	P_2O_5 in urine. Grams.	Uric acid in urine.[1] Gram.
1	7	817	15.38	2.98	....
2	7	902	13.89	3.07	....
3	7	993	14.28	3.21	0.37
4	7	838	13.68	3.23	0.32
5	2½	852	13.96	2.94	0.36
6	4	782	14.04	3.07	0.34
7	0	851	15.63	3.28	0.34
8	7½	966	15.06	3.80	0.30
9	7½	1160	15.65	3.46	0.31
10	7	978	13.67	3.07	0.34
11	7	952	13.51	2.89	0.32
12	7	1001	13.82	3.21	0.30

From this it would appear that the loss of sleep had little, if any, influence upon the elimination of uric acid.

INFLUENCE OF DIET AND MUSCULAR WORK.

While there is no question that the different nitrogenous bodies of the food differ greatly in their effect upon uric acid formation and that very little uric acid is formed on a diet of such foods as bread, milk, butter and eggs, it is still uncertain whether the uric acid output is entirely independent of the quantity of such foods consumed. The results of two series of observations upon subject "S," bearing upon this point, may be summarized as follows:

INFLUENCE OF VARYING AMOUNTS OF BREAD AND MILK.

Days.	Amount of urine. Grams.	Nitrogen in urine. Grams.	P_2O_5 in urine. Grams.	Uric acid in urine. Gram.	Food per day.
1	681	11.65	1.92	0.42	Bread ("soda-crackers"), 150 grams; milk, 1500 grams.
2	605	11.12	2.02	0.35	
3	620	11.35	2.27	0.37	
4	566	11.66	2.33	0.38	
5	555	11.75	2.29	0.38	
6	687	14.83	2.73	0.44	Bread ("soda-crackers"), 300 grams; milk, 3000 grams.
7	874	15.81	3.28	0.41	
1	...[2]	....	....	....	Bread ("soda-crackers"), 405 grams; milk, 1000 grams; butter, 60 grams.
2	609	10.19	2.15	0.32	
3	711	10.92	2.43	0.37	
4	670	10.17	2.34	0.33	
5	2180	15.12	3.39	0.33	Bread ("soda-crackers"), 120 grams; milk, 3060 grams.
6	2130	16.07	3.94	0.34	
7	1859	16.98	4.10	0.34	

[1] The figures for uric acid given in this and the following table were determined by Folin's modification of the Hopkins method.

[2] Sample lost.

In the first series, where the change consisted in doubling the amounts of bread and milk consumed, the relative proportions remaining the same, there appears to be a slight increase in the uric acid elimination. In the second series, where the diet was changed by omitting the butter, reducing the bread and greatly increasing the milk consumed, thus giving a large increase in the protein of the diet with but little change in the fuel value, the amount of uric acid eliminated remained practically unchanged.

The fact that the slight increase found in the first series does not appear in the second, may be taken as an indication either that the increase was due to the superabundance of the diet as a whole, rather than to the increased consumption of protein alone, or that the purin bodies, while occurring only in very small quantities in either, were relatively more abundant in the bread than in the milk. The latter seems probable, inasmuch as the quality of flour used in making "soda-crackers" might easily contain some of the germ of the wheat. In either case it would appear that even a diet of bread and milk introduces a certain amount of "exogenous" purin bodies, though this amount is doubtless quite small.

The large quantities of uric acid eliminated by the professional bicycle racers may, therefore, to some extent, be attributed to the mere abundance of the diet. To a much greater extent, however, it is doubtless due to the quantities of meat extract consumed. During a two days' experiment, the attempt was made by subject "S" to consume such quantities of meat, meat extract and fruit (together with bread and milk) as would be comparable with those found in the dietaries of two of the racers.[1] The food consumed by "S" during the two days was about as follows: Meat, 400 grams; meat extract, 100 grams; milk, 2000 grams; bread, 350 grams; fruit, 800 grams. Except as regards the quantities of cereal and milk products, this dietary is not greatly different from the average for subjects "M" and "P" during the first two days of the bicycle race, including the meat consumed by these subjects just before the beginning of the observations.

The principal source of purin bodies was, of course, the meat extract, a concentrated commercial preparation called "Vigoral."

[1] On account of the great variety of foods consumed by subject "A" and the fact that he took cocoa wine and, during the last days, small quantities of strychnine, no direct comparison with this subject was attempted.

"M" and "P" consumed respectively 127 and 85 grams (average 106 grams), while "S" consumed 100 grams of the same preparation. "S" eliminated, during the two days, 1.66 grams of uric acid, or 0.83 gram per day; "M" and "P" together 3.53 grams, or an average of 0.88 gram per day. This difference is hardly greater than would be expected from the large quantities of cereals and milk consumed by the latter subjects. Hence, in so far as this method of comparison is applicable, it would indicate that, at least during the early days of the race, the uric acid elimination of these athletes was only such as would naturally result from the food consumed and was not appreciably increased by the muscular work performed.

In another experiment, "S," who at this time was living upon a diet of cereals and milk, and had taken but little exercise for three or four weeks, walked two and one-half hours over country roads at the rate of four and one-half miles per hour and during the following two and one-half hours practiced, at intervals, an exercise consisting in raising and lowering the body by means of the arms. Nearly all of the muscles were thus exercised, and while the work performed was not large in actual amount, the exertion was sufficient to keep the pulse rate at 100 to 125 for about five hours and to cause a feeling of fatigue during the remainder of the day. The exercise was followed by an increase in the uric acid output of about 0.15 gram during the day of exercise and the day following. This result is in harmony with that reached by Dunlop, Paton, *et. al.*,[1] who found an increased elimination of uric acid after muscular exercise when the subject was in poor, but not when it was in good, training.

SUMMARY.

Without attempting a full discussion of the data here given, which would involve a review of the recent extensive investigations already mentioned, the principal points of interest may be summarized as follows:

Both with professional athletes and with the subject of sedentary habits, the elimination of uric acid was primarily dependent upon the food consumed.

While very small changes, apparently, resulted from large variations in the amount of a bread-and-milk diet, the elimination

[1] *J. Physiol.*, **22**, 68.

of uric acid was mainly determined by the quantities of meat products consumed.

In the case of well-trained professional athletes, very severe and prolonged muscular exertion had little influence upon the formation and elimination of uric acid, except indirectly, by inducing an appetite for stimulating foods such as meat extracts.

Marked loss of sleep had no apparent influence upon the amount of uric acid eliminated.

The writer desires to express his indebtedness to Professor W. O. Atwater, of Wesleyan University, in whose laboratory a large part of the work, here described, was performed.

NEW YORK CITY,
September, 1903.

[CONTRIBUTIONS FROM THE UNIVERSITY OF ILLINOIS, AGRICULTURAL EXPERIMENT STATION, NO. 10.]

THE CHEMICAL COMPOSITION OF DIFFERENT PARTS OF THE CORN[1] KERNEL.[2]

BY C. G. HOPKINS, L. H. SMITH, AND E. M. EAST.

Received September 8, 1903.

THE possibility of selecting seed corn for improved chemical composition by a simple mechanical examination of sections of kernels has been clearly established by experiments previously reported;[3] and the practical value of this method of selecting seed corn for high protein, high oil, and other desirable qualities, has been fully confirmed by subsequent investigations.[4]

A considerable amount of additional data relating to this matter has been accumulating with the progress of our experiments in corn-breeding, and because of the very great importance of this subject to agriculture, and also because of the marked interest which is manifested both by progressive, practical agriculturists and by scientific investigators, it has seemed advisable to publish, in somewhat greater detail, the results of our investigations along this line.

[1] "Corn" is, of course, used with the American meaning of Indian corn or maize.

[2] From advance sheets of Bulletin No. 87 of the University of Illinois Agricultural Experiment Station.

[3] This Journal **21**, 1039 (1899); Univ. of Ill. Agr. Expt. Station Bulletin **55** (1899).

[4] Univ. of Ill. Agr. Expt. Station Bulletin **82** (1902); U. S. Dept. of Agr., Office of Expt. Stations, Bulletin **123**, 91 (1903); West Indian Bulletin **4**, 9 (1903).

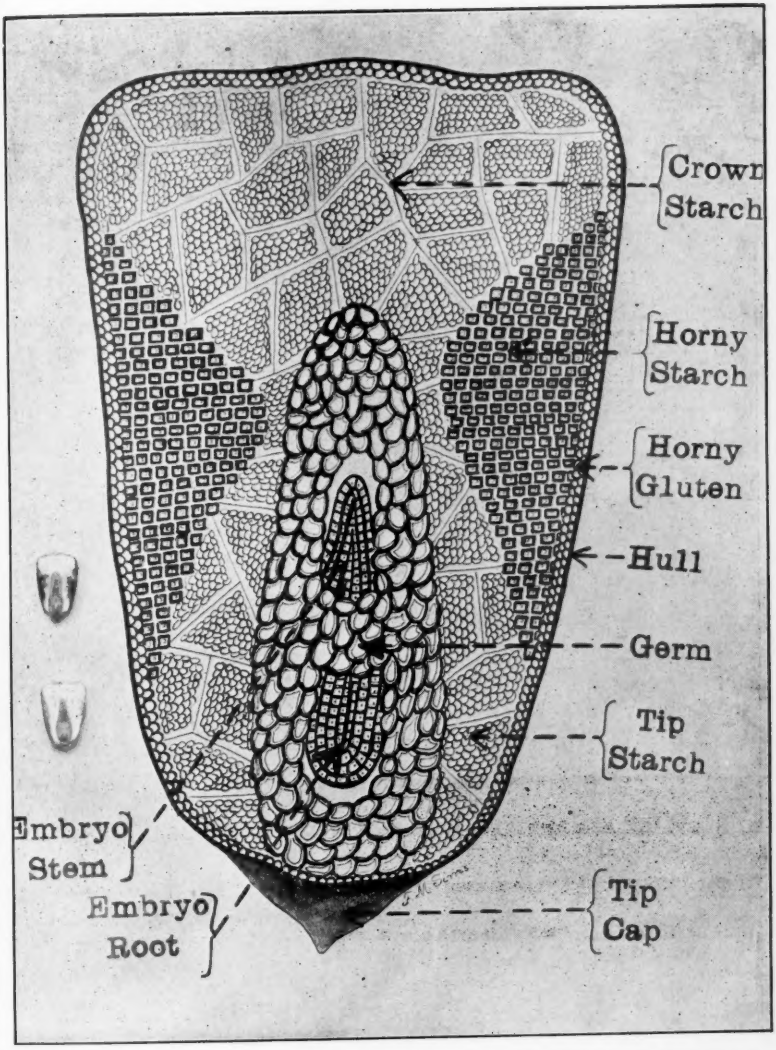

Plate I.—Low-protein corn kernel from drawing (small kernels from photograph).

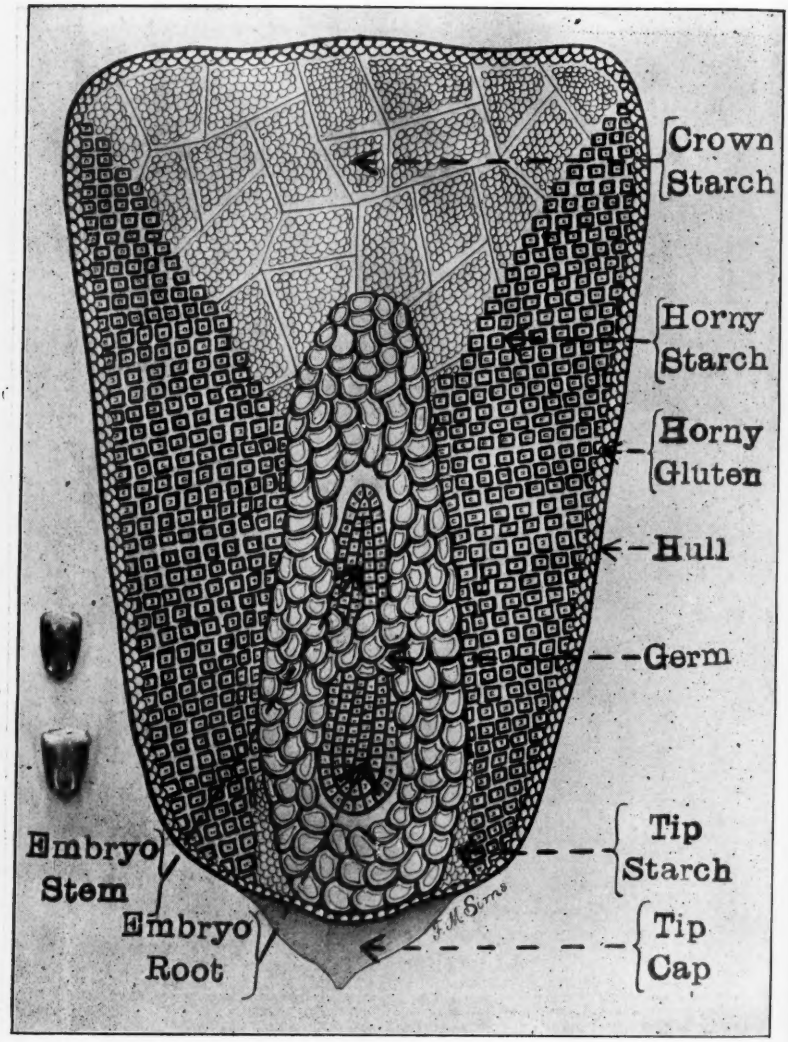

Plate II.—High-protein corn kernel from drawing (small kernels from photograph).

PARTS OF THE CORN KERNEL.

There are six distinctly different parts in a kernel of corn, as will be readily seen by the reference to Plates[1] I and II.

(1) *Tip Cap.*—This is a small cap, covering the tip end of the kernel, and serves as a protection to the end of the germ. It consists of material somewhat resembling the cob, and occasionally, in shelling corn, the tip cap remains attached to the cob, leaving the tip end of the germ uncovered, but nearly always it remains on the kernel.

(2) *Hull.*—This is the very thin outer covering of the kernel. It consists largely of carbohydrates, especially fiber or cellulose, although it also contains a small percentage of other constituents.

(3) *Horny Glutinous Part.*—This part is the aleurone layer which lies immediately underneath the hull. It constitutes a second covering of the kernel, usually much thicker than the hull. For short, it is called *horny gluten,* although it is, of course, not pure gluten. However, it is the richest in protein of any part of the corn kernel, as has been stated in bulletins published by this station and previously by Dr. Voorhees, director of the New Jersey Experiment Station.

(4) *Horny Starchy Part.*—This part lies next to the horny gluten, on the back and sides of the kernel. For short, it is called *horny starch,* although it is not pure starch, as it contains considerable amounts of other constituents, especially of protein. In an examination of the kernel with the unaided eye, the horny glutinous part and the horny starchy part are not readily distinguished from each other, the line between them being somewhat indefinite and indistinct. Considered both together, these two parts constitute the horny part of the kernel.

(5) *White Starchy Part.*—This part occupies the crown end of the kernel above the germ and it also nearly surrounds the germ toward the tip end of the kernel. For convenience, this material is called *white starch,* although it is not pure starch. In some kernels the horny starch extends nearly or quite to the germ (near the middle of the kernel) and thus separates more or less completely the white starch into two parts which we call *crown starch* and *tip starch.*

[1] It should be understood that these drawings are intended to show merely the location and relative amounts of the various parts of the kernel, not the exact cell structure.

(6) *Germ.*—The germ occupies the center of the front of the kernel toward the tip end and usually extends about one-half or two-thirds of the length of the kernel. Within the body of the germ are the embryo stem pointing upward toward the crown end and the embryo root pointing downward toward the tip of the kernel, both of which are, of course, parts of the germ. These embryo parts within the germ may be easily seen by any one who will carefully shave off the front side of the germ from a kernel of corn (see small photographic reproduction of sections of kernels of high- and low-protein corn in Plates I and II).

MECHANICAL SEPARATION OF THE DIFFERENT PARTS.

It is not a difficult matter to obtain very pure samples of each of the above-named parts of the corn kernel, although in making the separations there is, of necessity, some waste material consisting of a mixture of three different parts; namely, horny gluten, horny starch, and white starch.

By the use of a small, sharp knife, any one can make the following separations: (1) Tip cap; (2) hull; (3) horny gluten; (4) horny starch;[1] (5*a*) crown starch; (5*b*) tip starch; (6) germ; (7) waste (mixed material). In making these separations the kernels are first soaked in hot water for fifteen or twenty minutes.

The tip cap is then very easily and perfectly separated by simply cutting under one edge and then pulling it off. The hull is separated without difficulty by peeling it off in strips. It is only necessary to use the knife to start the peeling at the tip end where the hull has been broken by removing the tip cap. With some care the hull can be completely peeled out of the dent in the corn. The aleurone layer is more easily distinguished after the hull is removed. It covers the entire kernel, excepting the germ.[2] The aleurone layer is removed by carefully shaving it off with a sharp knife. Adhering particles of starch can be more easily separated from this horny gluten after the shavings have been allowed to dry for some time. In scraping off these particles of horny starch or white starch adhering to the shavings, more or less horny gluten will also be scraped off, so that, while we are thus able to obtain a pure, clean sample of the aleurone layer, we

[1] As used in this article the term "starch" is employed in a technical or commercial sense, and not as the name of a definite chemical compound.

[2] This layer does not occur between the germ and the tip cap as indicated in the drawings.

also obtain some waste material, consisting of particles of horny gluten, horny starch, and white starch.

The germ is next removed, and with care this can be done very perfectly. If any particles of starch adhere to the germ they can easily be completely removed. After the tip cap, hull, aleurone layer, and germ have been removed, the remainder of the kernel, consisting of the horny starch and white starch only, is allowed to dry, and the kernel is broken in two lengthwise.

The crown starch is dug out with the knife as completely as possible without taking any of the horny starch. The tip starch is next removed in the same manner as the crown starch. The horny starch from each side usually remains in a solid piece. This is now carefully scraped to remove all adhering particles of white starch or horny gluten, the scrapings being carefully saved and added to the waste material.

By this method of separation we obtain eight different products, including the waste material, and seven of these products are pure samples of distinctly different parts of the corn kernel, excepting the crown starch and tip starch, both of which, of course, belong to the white starch; they are kept separate, however, because they are found in different places, frequently being entirely separated in the kernel, although more commonly there is some white starch continuous from crown to tip.

COMPOSITION OF THE DIFFERENT PARTS.

Table I shows the percentage of these eight different products, or parts, and the percentage composition of each part, also the percentage composition of the whole corn, for each of three different ears of corn. Ear No. 1 is corn of comparatively low[1] protein content. Ear No. 2 has about the usual protein content of ordinary corn. Ear No. 3 is high[1] protein corn. About 200 grams (nearly one-half pound) of kernels from each ear were separated into the different parts, and each part was then weighed and

[1] It should be understood that ear No. 1 (9.28 per cent. protein) and ear No. 3 (12.85 per cent. protein) do not represent extremes in protein content; indeed, in our breeding of corn for low protein we have produced good ears containing less than 6.50 per cent. of protein, and in our high-protein field we have produced corn containing over 16 per cent. of protein. In extremely low-protein corn the percentage of horny part is very much less than in ear No. 1, and in extremely high protein corn the tip white starch is frequently almost entirely wanting and the crown white starch very greatly reduced, both being replaced by the horny part, as shown in the drawings and also in the actual photographs of sections of kernels shown beside the drawings in Plates I and II.

analyzed separately, another sample of the corn from each ear being analyzed to give the composition of the whole corn. (All results are given on the water-free basis.)

TABLE I.—PERCENTAGE OF DIFFERENT PARTS AND PERCENTAGE COMPOSITION OF EACH PART.

Names of parts.	Per cent. of whole.	Composition of parts. Protein. Per cent.	Oil. Per cent.	Ash. Per cent.	Carbohydrates. Per cent.
Ear No. 1 (low in protein).					
Tip caps	1.20	7.36	1.16	0.91	90.57
Hulls	5.47	4.97	0.92	0.82	93.29
Horny gluten	7.75	19.21	4.00	0.92	75.87
Horny starch	29.58	8.12	0.16	0.18	91.54
Crown starch	16.94	7.22	0.19	0.32	92.27
Tip starch	10.03	6.10	0.29	0.29	93.31
Germs	9.59	19.91	36.54	10.48	33.07
Mixed waste	18.53	9.90	1.06	0.61	88.43
Whole corn	....	9.28	4.20	1.41	85.11
Ear No. 2 (medium in protein).					
Tip caps	1.46	8.83	2.30	1.11	87.76
Hulls	5.93	3.96	0.89	0.79	94.36
Horny gluten	5.12	22.50	6.99	1.72	69.09
Horny starch	32.80	10.20	0.24	0.24	89.32
Crown starch	11.85	7.92	0.17	0.24	91.67
Tip starch	5.91	7.68	0.39	0.31	91.62
Germs	11.53	19.80	34.84	9.90	35.46
Mixed waste	25.40	11.10	1.23	0.57	87.10
Whole corn	....	10.95	4.33	1.55	83.17
Ear No. 3 (high in protein).					
Tip caps	1.62	4.64	1.99	1.87	91.50
Hulls	6.09	3.84	0.76	1.10	94.30
Horny gluten	9.86	24.58	4.61	1.74	69.07
Horny starch	33.79	10.99	0.22	0.21	88.58
Crown starch	10.45	8.61	0.52	0.37	90.50
Tip starch	6.23	7.29	1.36	0.60	90.75
Germs	11.93	19.56	33.71	10.00	36.73
Mixed waste	20.03	12.53	1.15	0.61	85.71
Whole corn	....	12.85	5.36	1.67	80.12

A careful study of Table I reveals some very interesting and useful facts regarding the structure of the corn kernel and the composition of the different parts. It is exceedingly useful to be able, by a mechanical examination of corn, not only to pick out high-protein corn or high-oil corn as one may desire, but even to separate the several distinctly different parts from one another

by purely mechanical means—to separate, for example, the aleurone layer, containing (in the high-protein ear) nearly 25 per cent. of protein, and then the white starchy parts, with only 7 or 8 per cent. of protein; or the germs containing about 35 per cent. of oil and 10 per cent. of ash, and then the horny starchy part containing less than 0.25 per cent. of either oil or ash.

The hulls contain about 4 per cent. of protein and are clearly the poorest in protein of any part of the kernel, the next poorest being the tip caps and white starchy parts, containing about 7 or 8 per cent., the tip starch being slightly poorer than the crown starch. The horny starch is richer in protein than the white starch, especially in the medium and high protein corn where the difference amounts to more than 2 per cent., the horny starchy part containing from 10 to 11 per cent. of protein. The protein content of the germs is very uniform in the different ears, although the poorest germs are found in the high-protein corn, and the richest in the low-protein corn, the variation being from 19.56 to 19.91 per cent. The aleurone layer is the richest in protein of any part of the kernel in both ordinary and high-protein corn, as was pointed out several years ago by Dr. Voorhees,[1] director of the New Jersey Experiment Station, and as we have quoted in previous publications of the Illinois Experiment Station. In the high-protein corn the protein content of the aleurone layer amounts to 24.58 per cent. In the low-protein corn it is slightly less than that of the germ.

It is plainly seen that the oil in corn is very largely in the germ, although the aleurone layer also contains a considerable percentage, the germ containing about 35 per cent. of oil and the aleurone layer about 5 per cent. Both the horny starch and the white starch are exceedingly poor in oil, averaging about 0.25 per cent., if we disregard the tip starch in ear No. 3, which appears to have absorbed some oil directly from the germ which it adjoins and partially surrounds. The hulls contain slightly less than 1 per cent. of oil and the tip caps slightly more than 1 per cent., and it is quite possible that this oil may have been obtained, in part at least, by absorption from the aleurone layer and germ. Indeed, it seems highly probable that practically all of the true oil in the corn kernel is originally deposited in the germ and aleurone layer.

[1] New Jersey Agricultural Experiment Station Bulletin **105** (1894).

and that the small percentage or mere trace, which is found in the other parts, is largely obtained by absorption. That such absorption actually does occur is definitely proved by the fact that the percentage of oil in hominy and hominy products increases with the age of the corn used in the milling. (Hominy consists largely of the horny starch with more or less adhering white starch.)

It may be of interest to state in this connection that in 1866 Haberlandt[1] discovered, with the microscope, that the germ of the corn kernel contains a large amount of oil. He observed no oil in the remaining portions of the kernel. By chemical analysis, Lenz[1] found, however, that after the germs were removed the remaining portion of the kernel contained 1.57 per cent. of oil. These results were fully confirmed by Dr. Atwater,[2] who found 1.63 per cent. of oil in the corn after removing the germs and adjoining material, although neither Lenz nor Atwater appear to have ascertained that the horny gluten (the aleurone layer) contains the chief percentage of oil outside of the germ.

By further reference to Table I, it will be observed (1) that the germ contains about 10 per cent. of ash or mineral matter; (2) that this is about ten times the average percentage of ash contained in the other parts; and (3) that the percentage of ash in the different parts varies with the percentage of oil, to quite a noticeable degree. Of course, the percentage of carbohydrates (starch, cellulose, pentosans, etc.) varies inversely as the sum of the other constituents, being about 35 per cent. in the germ, 70 per cent. in the horny gluten, and from 90 to 95 per cent. in the other principal parts.

The marked degree of uniformity in the entire percentage composition of the germs from each of these three ears, whether low-protein, medium-protein, or high-protein, seems especially noteworthy. The percentage of protein varies only from 19.56 to 19.91; the oil from 33.71 to 36.54; the ash from 9.90 to 10.48; and the carbohydrates from 33.07 to 36.73. It will also be noted that the percentages of both protein and oil are lower in the germs from high-protein corn than in those from the low-protein corn, although the differences are not marked.

[1] *Allgemeine land- und forstwirtschaftliche Zeitung*, 1866, p. 257; *Jahresbericht* (Hoffmann) *über die Agricultur-Chemie*, **9**, 106 (1866).

[2] Thesis, Yale College (1869); *Am. J. Sci. and Arts* (2). **48**, 352 (1869).

MATHEMATICAL DISTRIBUTION OF WASTE.

It will be borne in mind that in making the mechanical separations, in order to obtain each of the seven different parts in pure condition, unmixed with any other part, there was necessarily some waste product. This waste substance amounted to about 20 per cent. of the whole. As has already been explained, this mixed waste material consists of only three distinctly different parts—horny gluten, horny starch, and white starch (from crown and tip), the other three parts—tip caps, hulls, and germs—being easily separated completely and in pure form.

By a simple computation the mixed waste material can be distributed among the respective parts of which it is composed, provided we may be allowed to make the assumption (which is approximately the truth) that the horny starch and white starch are present in the waste material in the same proportions as they are in the pure separated portions. Any error which might be introduced by following this assumption would have but little effect because the composition of the horny starch and white starch are not very markedly different (the protein differs by 2 to 3 per cent.); and also because the total amount of waste material to be distributed is only from one-third to one-half the sum of the separated horny starch and white starch.

It will be observed (see Table I) that the mixed waste is always richer in protein than the horny starch, thus showing that, besides horny starch and white starch, it also contains more or less horny gluten, which, of course, we know to be the fact.

If in 100 grams of corn we let x equal the number of grams of tip starch, Bx the number of grams of crown starch, Cx the number of grams of horny starch, y the number of grams of horny gluten, and S the sum of these four parts, then

$$x + \mathrm{B}x + \mathrm{C}x + y = \mathrm{S}. \qquad (1)$$

Now if we let a equal the per cent. of protein in the tip starch, b the per cent. of protein in the crown starch, c the per cent. of protein in the horny starch, d the per cent. of protein in the horny gluten, and s the number of grams of protein in all of these four parts, then

$$ax + b\mathrm{B}x + c\mathrm{C}x + dy = s. \qquad (2)$$

Thus we have two equations with which to solve for x and y, which are the only unknown quantities, B and C being factors

which can be obtained by dividing the per cent. of separated crown starch and horny starch, respectively, by that of tip starch, and S being the sum of the separated tip starch, crown starch, horny starch, horny gluten and mixed waste, as given in Table I, and *a, b, c, d* being the respective percentages of protein in the four separated materials, tip starch, crown starch, horny starch, and horny gluten, and *s* being the total number of grams of protein contained in these four separated parts and in the mixed waste, all of which data are also given in Table I.

PHYSICAL COMPOSITION OF THE CORN KERNEL.

From the above computations we obtain the results given in Table II, which gives the total percentages of each of the seven different parts contained in the corn kernel (counting crown starch and tip starch as two parts), and with no waste material.

TABLE II.—TOTAL PERCENTAGES OF THE DIFFERENT PARTS OF THE CORN KERNEL.

Name of parts.	Ear No. 1 (low-protein).	Ear No. 2 (medium-protein).	Ear No. 3 (high-protein).
Tip caps	1.20	1.46	1.62
Hulls	5.47	5.63	6.09
Horny gluten	11.61	8.51	13.32
Horny starch	37.15	47.08	44.89
Crown starch	21.26	17.01	13.88
Tip starch	13.71	8.48	6.28
Germs	9.59	11.53	11.93
Total	99.99	100.00	100.01

It will be observed that the percentages of horny gluten, horny starch, and germs are noticeably higher in the high-protein corn than in the low-protein corn, while the opposite is true with the white starch, the percentages of crown starch and tip starch being markedly higher in the low-protein corn than they are in the high-protein corn. It is noteworthy that the horny gluten in high-protein corn not only contains a higher percentage of protein than the germs, but that the proportion of horny gluten in the kernel equals or exceeds that of the germs. The only discrepancies appearing in Table II are the low percentage of horny gluten and the high percentage of horny starch in ear No. 2. Otherwise the percentages of parts in the medium-protein ear are always intermediate between those in the other two ears, as would be expected. Even these discrepancies disappear if the two

horny parts be added together and considered as one part, as is done in the practical work of selecting seed corn for higher protein content by mechanical examination, as will be seen by referring to Table III.

TABLE III.—PERCENTAGES OF THE DIFFERENT PARTS OF THE CORN KERNEL AS COMMONLY OBSERVED IN MECHANICAL EXAMINATION FOR SEED CORN SELECTION.

Name of parts.	Ear No. 1 (low-protein).	Ear No. 2 (medium-protein).	Ear No. 3 (high-protein).	Average. Per cent.
Tip caps	1.20	1.46	1.62	1.43
Hulls	5.47	5.93	6.09	5.83
Horny part	48.76	55.59	58.21	54.19
White starch	34.97	25.49	22.16	27.54
Germs	9.59	11.53	11.93	11.02
Total	99.99	100.00	100.01	100.00

In this table the crown starch and tip starch are also added together and the sum recorded as white starch. The increase in the amount of horny part (from 48.76 to 58.21 per cent.) and the decrease in white starch (from 34.96 to 22.16 per cent.) as we pass from the low-protein to the high-protein corn, is plainly apparent.

DISTRIBUTION OF CHEMICAL CONSTITUENTS.

Table IV shows the location or complete distribution of the chemical constituents among the seven different physical parts of the corn kernel. In other words, this table represents the separation of 100 grams (or 100 pounds) of corn into seven different structural or physical parts, and the subsequent division of each of these parts into four chemical constituents, protein, oil, ash, and carbohydrates.

TABLE IV.—PHYSICAL AND CHEMICAL DISTRIBUTION OF 100 GRAMS (OR 100 POUNDS) OF CORN.

Ear No. 1 (low in protein).

Names of parts.	Physical distribution (grams or pounds).	Chemical distribution. Protein (grams or pounds).	Oil (grams or pounds).	Ash (grams or pounds).	Carbohydrates (grams or pounds).
Tip caps	1.20	0.09	0.01	0.01	1.09
Hulls	5.47	0.27	0.05	0.04	5.10
Horny gluten	11.61	2.23	0.46	0.11	8.81
Horny starch	37.15	3.02	0.06	0.07	34.01
Crown starch	21.26	1.53	0.04	0.07	19.62
Tip starch	13.71	0.84	0.04	0.04	12.79
Germs	9.59	1.91	3.50	1.01	3.17
Total	99.99	9.89	4.16	1.35	84.59
Whole corn	....	9.28	4.20	1.41	85.11

Ear No. 2 (medium in protein).

Names of parts.	Physical distribution (grams or pounds).	Chemical composition. Protein (grams or pounds).	Oil (grams or pounds).	Ash (grams or pounds).	Carbohydrates (grams or pounds).
Tip caps	1.46	0.13	0.03	0.02	1.28
Hulls	5.93	0.23	0.05	0.05	5.60
Horny gluten	8.51	1.89	0.59	0.15	5.88
Horny starch	47.08	4.80	0.11	0.11	42.05
Crown starch	17.01	1.35	0.03	0.04	15.59
Tip starch	8.48	0.65	0.03	0.03	7.77
Germs	11.53	2.28	4.02	1.14	4.09
Total	100.00	11.33	4.86	1.54	82.26
Whole corn	....	10.95	4.33	1.55	83.17

Ear No. 3 (high in protein).

Tip caps	1.62	0.08	0.03	0.03	1.48
Hulls	6.09	0.23	0.05	0.07	5.74
Horny gluten	13.32	3.27	0.61	0.23	9.20
Horny starch	44 89	4.93	0.10	0.09	39.76
Crown starch	13.88	1.20	0.07	0.05	12.56
Tip starch	8.28	0.60	0.11	0.05	7.51
Germs	11.93	2.33	4.02	1.19	4.38
Total	100.01	12.64	4.99	1.71	80.63
Whole corn	....	12.85	5.36	1.67	80.12

The agreement between the sum of the separate determinations and the direct determinations of the same constituent in the whole corn is very satisfactory, considering that these results are obtained by computation from the analyses of nine different materials, including the whole corn. The greatest difference is well within the limit of unavoidable error in sampling and analytical determinations. A careful study of this table will reveal some interesting and valuable facts. For example, it will be seen that in 100 pounds of the low-protein corn the horny gluten contains only 2.23 pounds of protein, while 3.27 pounds of protein are contained in the horny gluten in 100 pounds of the high-protein corn. Again, in 100 pounds of the low-protein corn the horny starch contains only 3.02 pounds of protein, while 4.93 pounds of protein are contained in the horny starch in 100 pounds of the high-protein corn.

On the other hand, in 100 pounds of the low-protein corn, the crown starch and tip starch contain 1.53 and 0.84 pounds of protein, respectively, while 1.20 and 0.60 are the respective amounts contained in the corresponding parts of the high-protein corn.

If we add together the horny parts and then add together the crown starch and tip starch, as is done in the practical selection of seed corn by mechanical examination, we obtain the results shown in Table V.

TABLE V.—POUNDS OF PROTEIN IN 100 POUNDS OF CORN.

Name of parts.	Low-protein corn.	Medium-protein corn.	High-protein corn.
In tip caps	0.09	0.13	0.08
In hulls	0.27	0.23	0.23
In horny part	5.25	6.69	8.20
In white starch	2.37	2.00	1.80
In germs	1.91	2.28	2.33
Total	9.89	11.33	12.64

It will be observed that the increase in protein in high-protein corn over that in low-protein corn occurs almost entirely in the horny part of the corn kernel. There is also a slight increase in protein in the germ, although this is quite insignificant as compared with the increase in the horny part. In passing from low-protein corn to high-protein corn, there is an appreciable decrease in the amount of protein contained in the white starch. Of course, this is due to the marked decrease in the actual amount of white starch in high-protein corn. Indeed, this decrease in the quantity of white starch is even more marked than would appear from Table V, because the white starch in the high-protein corn is actually richer in protein than that in low-protein corn, as would be expected and as is shown in Table I.

The data given in Table V strongly confirm the results which we have already obtained in practical experience in corn-breeding. For example, we have been breeding both high-protein corn and low-protein corn for the past seven years. In the high-protein corn we find that the proportion of horny part has increased very markedly, while the white starchy part has markedly decreased. In the low-protein corn the opposite is true, the horny part having decreased and the white starchy part having markedly increased, in proportion.

By computation from the data given in Table IV, we have constructed Table VI, which shows the percentage distribution of the different chemical constituents among the several physical parts of the corn kernel.

TABLE VI.—PERCENTAGE DISTRIBUTION OF CHEMICAL CONSTITUENTS AMONG PHYSICAL PARTS.

Ear No. 1 (low in protein).

Name of parts.	Per cent. of total protein.	Per cent. of total oil.	Per cent. of total ash.	Per cent. of total carbohydrates.
In tip caps	0.89	0.33	0.81	1.29
In hull	2.75	1.21	3.34	6.03
In horny gluten	22.56	11.13	7.96	10.41
In horny starch	30.51	1.43	4.98	40.22
In crown starch	15.52	0.97	5.07	23.18
In tip starch	8.46	0.95	2.96	15.12
In germs	19.31	83.99	74.87	3.75
Total	100.00	100.01	99.99	100.00

Ear No. 2 (medium in protein).

In tip caps	1.14	0.69	1.06	1.56
In hull	2.07	1.08	3.06	6.80
In horny gluten	16.67	12.21	9.56	7.15
In horny starch	42.36	2.32	7.38	51.12
In crown starch	11.88	0.59	2.67	18.96
In tip starch	5.75	0.68	1.72	9.45
In germs	20.14	82.43	74.55	4.97
Total	100.01	100.00	100.00	100.01

Ear No. 3 (high in protein).

In tip caps	0.59	0.65	1.76	1.84
In hull	1.85	0.93	3.90	7.12
In horny gluten	25.88	12.29	13.49	11.41
In horny starch	39.00	1.98	5.49	49.31
In crown starch	9.45	1.44	2.99	15.58
In tip starch	4.77	2.25	2.89	9.32
In germs	18.45	80.46	69.46	5.43
Total	99.99	100.00	99.98	100.01

It will be seen that as an average about 22 per cent. of the total protein is contained in the horny gluten, nearly 40 per cent. in the horny starch, and nearly 20 per cent. in the germ; thus these three parts contain about 80 per cent. of the total protein in the kernel.

The germ contains from 80 to 84 per cent. of the oil, while all other parts combined contain only 15 to 20 per cent. of the total oil in the kernel. Based upon this fact is the method for selecting high-oil or low-oil seed corn by mechanical examination, the ears whose kernels show a large proportion of germ being high-

oil corn and those with small germs, low-oil corn. About 12 per cent. of the total oil is contained in the aleurone layer, leaving only about 5 per cent. of the oil distributed among the remaining five physical parts, and, as stated above, more or less of this small amount is undoubtedly absorbed from the contiguous germ or aleurone layer. It will be noted that the ash is closely associated with the oil, nearly 75 per cent. of the total ash being contained in the germ, and about 10 per cent. in the aleurone layer as an average.

Table VII shows, for direct comparison, the percentage distribution of the protein among the different physical parts, in each ear, the two horny parts, and also the two white starchy parts, being combined as in Table V.

TABLE VII.—DISTRIBUTION OF 100 GRAMS (OR 100 POUNDS) OF PROTEIN AMONG THE PHYSICAL PARTS AS OBSERVED IN MECHANICAL EXAMINATION.

Names of parts.	Low-protein corn.	Medium-protein corn.	High-protein corn.
In tip caps	0.89	1.14	0.59
In hulls	2.75	2.07	1.85
In horny part	53.07	59.03	64.88
In white starch	23.98	17.63	14.22
In germs	19.31	20.14	18.45
Total	100.00	100.01	99.99

Table VII illustrates very plainly the fact that, as we pass from low-protein corn to high-protein corn, the protein decreases in the white starchy part and increases in the horny part; in other words in breeding corn for high protein, we decrease the white starchy part, which is comparatively poor in protein, and increase the horny part, which averages very much richer in protein, the horny starch containing 2 to 3 per cent. more protein than the white starch, and the horny gluten (aleurone layer) being richer in protein than any other part of the kernel. As a rule, in breeding for high protein there is also a slight increase in the proportion of germ, which, being rich in protein, adds somewhat to the increase in protein.

CRITICAL REVIEW OF THE SECOND SERIES OF ANALYSES OF MATERIALS FOR THE PORTLAND CEMENT INDUSTRY MADE UNDER THE AUSPICES OF THE NEW YORK SECTION OF THE SOCIETY OF CHEMICAL INDUSTRY.

By W. F. Hillebrand.

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The efforts of a committee of the New York Section of the Society of Chemical Industry, headed by Mr. Clifford Richardson, to improve the state of technical analysis in this country are doubtless known to many, if not most readers of this Journal. The subjects thus far taken up have been Portland cement and copper slag analysis, the latter initiated by Mr. Thorn Smith, of Isabella, Tennessee. Carefully prepared samples were sent to many chemists and the tabulated results of analysis were handed over to me for examination and criticism. A report on each subject was rendered. The first, on Portland cement and raw limestone mixture, was published as a part of the Committee's report in the *Journal of the Society of Chemical Industry*, January 15, 1902.[1] In the number of October 15, 1902, there is a criticism of it by Messrs. Stanger and Blount, with attendant discussion by others. The report on copper slag analyses has not appeared in print, but in the *Engineering and Mining Journal*, **75**, 295, the list of analyses is given with extended comments by Mr. Thorn Smith, based upon this report, of which copies had been sent to the gentlemen who had made the analyses. Following the first cement report, which contained a tentative scheme for technical analysis by the committee, a second series of samples was distributed for analysis in accordance with its directions. Upon the data thus secured, a second report was rendered by me to Mr. Richardson, and at his request I have prepared, for publication, the present paper, which contains the greater part of that report in practically its original form. In preparing the report, much chemical work was done in the laboratory of the United States Geological Survey, the results of which were tabulated and discussed, but, however interesting they may be from some points of view, they are not all of sufficient importance to warrant the consumption of space required for their presentation herein.

[1] This Journal, **23**, R 289.

A cursory glance over the tabulated results of the present series of analyses offers little encouragement to those who hoped for a decided improvement over the first series made in 1901. But it requires no very critical examination to show that there is improvement in certain directions and that the outlook is not all dark. It is unfortunate for the purposes of a satisfactory review of the data presented that the committee's provisional scheme of analysis allowed any discretion as to whether certain corrections throughout the analysis should be made or not; for instance, the correction of silica by hydrofluoric and sulphuric acids, of alumina by potassium acid sulphate, and in the matter of double precipitation of alumina, lime, and magnesia. Thus, while nearly all the chemists practiced double evaporation and filtration for silica and almost all of these blasted silica, but thirteen applied the hydrofluoric acid correction; fifteen precipitated lime twice, but only eleven took the same precaution with magnesia. It would have been more satisfactory had the samples been sent only to those having adequate facilities and agreeing to faithfully carry out the analyses according to a strictly laid down procedure, from which no important deviation could be allowed. Then, and then only, could the results be thoroughly comparable and admit of plain deductions. As it is, so few have adhered throughout to the committee's recommendations that the task of sifting the data has been very arduous and the results by no means commensurate with the labor expended.

This last statement is strengthened by the fact, revealed by special inquiries during the last stages of the examination, that the water used by a number of chemists was so impure as to vitiate their analyses as to certain constituents. Only a few gave quantitative data on the quality of the water used by them, although information on this point was requested of all, but from the replies received it is manifest that not a few of the poor results are directly attributable to this cause and that the quality of the water used is often shamefully bad. One chemist, in fact, declined to undertake the analyses at all because of the poor quality of the only water that was at his service. Another analyst (*2*), after sending in his report and finding that his water yielded, on evaporation, 16.7 mg. per liter of residue—chiefly magnesium chloride and sulphate—repeated his analysis in duplicate with pure water and reported the results under *2a*, Tables II

and III. This showing makes it probable that his results in the 1901 series of analyses were affected by errors due to the same cause. Other chemists report up to 11 mg. of residue per liter, which, however, in some cases seems to be largely of organic nature or to consist of ammonium salts, since it disappears wholly or is reduced in weight after ignition. Some simply say the water used by them is good, others "do not know."[1] Even in the former case it may be questioned if, in lack of quantitative determinations, the statements as to quantity can be always unreservedly accepted, for the technical chemist is often too prone to dismiss, as negligible and unweighable amounts which may, nevertheless, be of moment in work of the present character. In illustration, I may mention that one or two, after evaporation of a solution containing silica, iron, alumina, etc., to dryness, and correction of the filtered silica by hydrofluoric acid, find "no residue." To one who has had much experience in silicate analysis, this is a wholly incredible statement, though it may be admitted that in cement analysis, by the exercise of unusual care, the amount of this residue may at times be very trifling.

The factor of the quality of the water and reagents has hitherto, perhaps, received too little attention. It was assumed by myself in my former report that the reagents used were of a degree of purity such as to affect the analyses with no serious error. Furthermore, perhaps their solvent action on the glassware employed for precipitations and evaporations was given insufficient weight. Mr. Thorn Smith, in a communication addressed to Mr. Richardson regarding a matter only indirectly connected with the present, comments on the very large amount of silica introduced into the iron precipitate from the beakers used by him in slag analysis. Such sources of error no doubt show their effect in the analyses of the present series, but it is in no case except No. 2 possible to indicate with certainty the analyses or parts of analyses thus affected, and too often it is not apparent how any error of this kind can be made an excuse for the wide variations ob-

[1] In this connection a paragraph from a report "The Examination of Foods, Drugs and Public Water Supplies," from the laboratory of hygiene of the State of New Jersey, by R. O. Brooks, recently published, is most pertinent "Fifty-seven samples of what purported to be distilled water were received and analyzed, only twelve of which were pure and only twenty-two of which had any claim to the title 'distilled water.' The residues ranged from 260 parts(!) per million to 8 parts, sixteen being above 100 parts and the average being 82 parts. All the samples with the exception of the aforementioned twenty-two gave tests for either chlorides, sulphates, calcium salts, carbonates or metallic impurities, usually several of these being present in one sample."

served. Total iron, for instance, should be susceptible of exact determination, yet the two series of cement analyses and the one of copper slag reported show a most lamentable state of affairs among chemists, which can, so far as I am able to see, be ascribed only to gross carelessness either in manipulation or preparation and care of standard solutions, for errors from the sources above mentioned would seem to be here excluded. If such carelessness has been shown with reference to iron, the inference is literally forced upon us that some of the other wide variations from the standard are due to similar causes. Some of these points will receive later consideration.

Because of the uncertainties above set forth, particularly as to the quality of the water, the labor expended in the preparation of this report has been in part wasted, but some of the observations made, are, as said earlier, not without value. It is quite useless, however, to continue experiments of this kind with reagents of doubtful quality.

The slurry and cement were not analyzed by me upon receipt from the Sandusky Portland Cement Co., but only six months later, after arrival of the reports from other analysts, and when it became apparent that without a standard analysis for comparison no adequate discussion of the data was possible.

The samples were received in glass vessels secured by a metallic screw-top pressing upon a cork washer. It does not seem probable that in the interim, during which the vessels remained unopened, there could have been a material absorption of carbon dioxide and water, though the ease with which such absorption can and does take place through apparently tight joints is too little appreciated. This view was not at first held, but the following experiment on the rate of absorption by the cement is instructive. A portion of the cement was placed in a platinum crucible and left in the balance case (which contained no drier) with the cover somewhat displaced. The weight was taken at intervals and the contents of the crucible disturbed from time to time, so as to expose fresh surfaces. The following are the results:

Weight of cement, 1.6853; weight of cement and crucible, 26.5515.

Weight after 1st day	26.5537	Weight after 11th day	26.5615
Weight after 2nd day	26.5548	Weight after 14th day	26.5631
Weight after 4th day	26.5573	Weight after 17th day	26.5633
Weight after 6th day	26.5592	Weight after 23d day	26.5637
Weight after 8th day	26.5602	Weight after 63d day	26.5642

There is shown a total gain during two months of but 0.75 per cent. when nearly fully exposed to the air. Even though this gain took place almost wholly early in the time period, it is not probable that in the closed vessel an appreciable increase of weight occurred. This conclusion is important, for, if true, it excludes as a probable source of serious error in this series of analyses that due to unequal absorption of carbon dioxide and water by the different samples of cement analyzed. It will be remembered that in the first series of analyses this was held to be a not improbable cause of the wide differences in "ignition loss" on the cement, an opinion which has lost most of its force, in view of the experiment referred to later under *Ignition Loss* (p. 1198).

The analyses made as standards of comparison head the lists given below. Their values are usually the mean of several closely agreeing determinations for which not quite the same degree of accuracy is claimed as for those made in 1901. In addition, others were made to test the committee's analytical scheme and the effect of using glass and porcelain vessels. From the first it appears that the committee's scheme is well adapted to furnish results that afford entirely satisfactory agreement with the standard, a conclusion which is confirmed by the concurrent testimony of several of the analysts who participated in the first series and who have since reported to the committee their experience with the method.

In this connection it may be as well to note that in my subsequent discussion I shall take into consideration some of the criticisms offered by Messrs. Stanger and Blount in their paper already referred to, and to which I, in part, replied at the time of its presentation in New York. A few of the criticisms and suggestions are, in my opinion, valid and good, and may well be heeded, should it seem fit in the light of experience to modify the committee's analytical procedure. Here it is incumbent upon me to point out that Mr. Blount and a number of others have fallen into error in thinking that the committee's method was devised by myself. Although it was submitted to me for comment and criticism and most of my suggestions were adopted, others were not. I purposely refrained from assuming the responsibility of devising a procedure to be followed by a class of factory chemists with whose laboratory facilities and general environment I had

no acquaintance. The scheme having been submitted to me for criticism, I made certain suggestions on what seemed to me the line of improvement from the chemical side chiefly, and there my responsibility ends. This is not to say that in my estimation the procedure is incapable of affording exact results when carefully followed (pure water and chemicals being assumed), for the contrary has been proved by myself and others. It was, however, admittedly a tentative scheme of analysis, open to and probably susceptible of betterment, in the matter of time at least. Mr. Blount has done us all a service in pointing out, in part, the way thereto. In the proper place I, too, shall indicate wherein modifications may, with advantage, be made both in view of certain suggestions of Mr. Blount and as a result of numerous experiments by myself on the slurry and cement samples now under discussion.

The standard analyses were made in general accordance with the outline of procedure given by me in my first report of 1901, but without regard to most of the minor constituents, except to ascertain that they were not present in such amounts that neglect to determine them would introduce errors of importance. Phosphorus and titanium are both present, but are counted in the analysis as alumina. No distinction is made between the different conditions of iron, but all is given as ferric oxide. Manganese is present, but in amount not to exceed 0.05 per cent. Its effect on the lime and magnesia figures has been ignored. Sulphur exists in both slurry and cement as sulphate and sulphide, the latter passing by ignition into sulphate without any loss at all, if the heat is not too prolonged or too high. This last subject is discussed further on in connection with the ignition loss (p. 1198). The alkali percentages are given because these constituents have an important bearing in explaining some of the variations for "loss on ignition," as will appear later (p. 1200).

The slurry was converted, in not over fifteen minutes, by a good blast, into a cement yielding but 0.05 per cent. of matter insoluble in hydrochloric acid. The contrary experience of some of the analysts is due solely to an ineffective blast or an improper manner of applying it, as with the crucible uncovered. The cement, when briefly treated with hydrochloric acid, yielded only 0.09 per cent. of insoluble matter after freeing from some separated silica, which amount might have been lessened perhaps by longer

action of the acid. These slight amounts of insoluble matter from both slurry and cement have not been entered separately, but were weighed with the silica, and what may have been left of them after correction by hydrofluoric acid was carried over to the alumina and iron. The error due to the possible presence in them of lime or magnesia is very slight indeed.

TABLE I.—STANDARD ANALYSES OF SLURRY AND CEMENT.

SO_3	1.43	1.82 SO_3[1]	1.53
S	0.16		0.09 } 1.75 SO_3
SiO_2	13.51		21.93
Al_2O_3	[2]3.50	4.93	[3]5.99
Fe_2O_3	1.43		2.35 } 8.34
CaO	40.84		62.92
MgO	0.75		1.10
K_2O	0.79		0.61
Na_2O	0.22		0.29
H_2O	4.20		1.40
CO_2	...		1.73
Ignition	...		2.91[4]

TABLE II.—ANALYSES OF SLURRY.

Standard.	SiO_2. **13.51.**	Al_2O_3-Fe_2O_3. **4.93.**	Al_2O_3. **3.50.**	Fe_2O_3. **1.43.**	CaO. **40.84.**	MgO. **0.75.**	SO_3. **1.43.**	Ignition loss. **37.50.**
1	(12.69)	(7.07)	.....	.....	(40.46)	(0.72)	.....	36.36*
2	(13.24)	(5.36)	(3.51)	(1.85)	(41.06)	(1.25)	(1.62)	39.62†
2*a*	13.46	5.00	3.77	1.23	40.90	0.79	1.42	37.46
	13.54	4.98	3.75	1.23	40.80	0.73	....	37.46
3	13.95	4.97	3.01	1.96	40.95	0.81	....	38.66
4*a*	13.78	4.94	3.28	1.66	41.42	0.62	....	38.84
4*b*	13.80	4.84	...	...	41.48	0.88	....	38.90
5	12.62	5.32	4.07	1.25	40.96	0.92	....	38.88
6	(12.96)	5.30	...	...	41.04	0.65	....	39.68
7	(15.00)	(4.61)	(2.58)	(2.03)	(42.13)	(1.25)	1.62	38.58
8	(15.54)	(4.90)	(3.76)	(1.14)	(42.27)	(1.50)	1.52	39.20
9	(12.76)	(5.51)	(4.13)	1.30	41.98	0.77	1.48‡	38.90
10*a*	13.39	5.22	...	...	40.96	0.88	...	37.32
10*b*	13.16	5.31	...	...	40.93	0.85	...	....
11	13.20	5.98	3.75	2.23	40.21	1.20	1.62	37.69
12	13.72	5.28	3.68	1.60	41.18	0.79	...	....
13	12.88	5.02	2.36	2.66	40.50	0.86	...	39.04
14§	12.10	5.10	...	...	41.00	0.90	1.75	37.38
15	13.55	5.02	...	...	41.40	0.79	...	....
16	12.78	6.22	...	...	41.18	1.07	...	37.48
17	13.38	5.14	...	...	42.17	0.82	1.43	37.32
18	12.61	5.53	3.77	1.76	41.26	1.33	1.54	37.78
19**	(14.91)	(4.20)	(3.02)	1.18	41.71	1.10	1.48	35.15

[1] By fusion, after slow ignition and subsequent extraction by HCl, there was found the same total—1.82.

[2] TiO_2, 0.18.

[3] TiO_2, 0.31.

[4] Mean of many results. The calculated loss from H_2O,CO_2, and the difference between 2FeS and Fe_2O_3.$2SO_3$ is 2.99. The slight discrepancy between the calculated and determined values may well be due to errors in the H_2O and CO_2 rather than in the directly found value for loss.

4*a*. Committee's method. 4*b*. Analyst's method. 7 and 8. Different analysts at same works. 10*a*. Committee's method. 10*b*. Analyst's method. * Average of five determinations. † Including 1.03 SO_3. ‡ Also 0.10 S. § Also 0.77 K_2O and 0.45 Na_2O. ** The figures of 19 are not in the form reported by the analyst, who gave analyses of soluble and insoluble parts separately.

TABLE III.—ANALYSES OF CEMENT.

Standard.	SiO_2. **21.93.**	Al_2O_3-Fe_2O_3. **8.34.**	Al_2O_3. **5.98.**	Fe_2O_3. **2.35.**	CaO. **62.92.**	MgO. **1.10.**	SO_3. **1.54.**	Ignition. loss. **2.91.**
1	22.29	9.68	....	....	62.81	0.95	1.52*	2.37†
2	(22.38)	(9.54)	(6.46)	(3.08)	(62.98)	(1.60)	(1.73)	2.66
2*a*	22.08	8.44	6.18	2.26	62.90	1.11	1.54	....
	22.04	8.50	6.20	2.30	62.80	1.15	....	....
3	22.10	8.72	5.78	2.94	63.44	1.23	1.52	2.71
4*a*	21.70	8.60	6.06	2.54	63.56	1.37	1.51	2.84
4*b*	21.68	8.46	....	....	63.56	1.25	1.52	2.85
5	21.20	9.04	6.67	2.37	63.13	1.39	1.58	3.48
6	22.08	8.66	....	....	63.09	1.31	1.63	3.74
7	(22.86)	(9.21)	(6.15)	(3.06)	(63.96)	(2.82)	1.56	....
8	(22.02)	(9.25)	(6.64)	(2.61)	(64.43)	(2.62)	1.38	....
9	21.69	8.64	6.19	2.45	63.27	1.08	1.43‡	4.50
10*a*	21.86	8.83	6.35	2.48	63.49	1.19	1.59	2.96
10*b*	21.79	8.83	6.35	2.48	63.40	1.20	....	....
	21.71	8.89	6.36	2.53	63.40	1.21	....	....
11	22.27	8.83	6.24	2.59	62.53	1.21	1.57	3.30
12	22.32	8.64	6.19	2.45	63.40	1.64	1.55	....
13	21.88	9.18	4.88	4.30	63.01	1.38	1.61§	2.66
14**	20.50	8.41	....	....	62.60	1.20	2.26	4.20
15	22.44	8.62	....	....	62.14	1.02	1.55	2.32
16††	22.18	8.52	....	....	63.88	1.28	....	2.86
17	22.24	8.36	....	....	63.72	0.99	1.46	3.01
18	22.58	9.08	6.48	2.60	63.15	1.38	1.51	2.58
19	22.53‡‡	8.39	5.74	2.65	63.88	1.34	1.62	0.98

4*a*. Committee's method. 4*b*. Analyst's method. 7 and 8. Different analysts at same works. 10*a*. Committee's method. 10*b*. Analyst's method. * Also 0.06 S. † Mean of two concordant results. ‡ Also 0.10 S. § Also 0.19 S. ** Also 0.85 K_2O and 0.50 Na_2O. †† Mean of close duplicates. ‡‡ In addition 0.20 insoluble in HCl reported.

Examination of the data furnished by most of the chemists with their analyses shows that certain of the latter must be rejected, in part at least, as not made in accordance with the committee's specifications in essential details. Slight deviations which could hardly affect the results appreciably, if at all, have not been regarded as sufficient ground for exclusion. This rule affects certain of the slurry analyses, and the values which are

regarded as fitly thrown out appear bracketed in the accompanying tables. With fuller information it is likely that still other figures would be similarly treated.

The grounds for excluding from discussion the bracketed values are the following:

Nos. 1 and 16.—The chemists, being unable to secure complete conversion to a soluble state by ignition, treated the partially converted slurry with hydrochloric acid, and, instead of filtering and further handling the residue as directed by the committee, evaporated silica and insoluble as for silica alone and corrected by hydrofluoric and sulphuric acids. No. 1 then found, after ignition, a fixed residue of 2.37 per cent., and No. 16 one of 2.60 per cent., which was, in each case, deducted from the crude silica and added to the alumina and ferric oxide obtained by precipitation with ammonia. Hereby a serious error was committed, affecting not only the value for silica, but those for alumina, lime, and perhaps magnesia as well, for the residue consisted not simply of aluminum and iron oxides, but of a little magnesia and probably considerable calcium sulphate too. The silica is thus made to appear too low by the amount of SO_3 retained by the lime, for, in case of No. 1, at least, the blast temperature was insufficiently high to convert to oxide. The lime and magnesia are also too low, but the alumina too high by the extent of the calcium sulphate and magnesia in the residue from the silica. In this way the quite abnormally high values for alumina and ferric oxide can be, in part at least, accounted for, but it is singular that analyst No. 1 should be the one to report also the highest alumina and ferric iron in the cement, where the conditions were normal and his silica and lime are nearly correct.

No. 2.—This analyst, after reporting, found that his water carried 16.7 mg. of solid matter to the liter, in large part chloride and sulphate of magnesium. His silica and lime values, particularly the latter, do not seem to be materially affected by the impurity of the water, but it has been thought best to reject the entire analyses for both slurry and cement. The analyses under *2a* are the work of the same analyst when using pure water, but as they were made after seeing the standard analyses, it is not right to consider them in the discussion.

No. 6.—In this case the insoluble and silica were fused with sodium carbonate, but instead of adding the hydrochloric acid solution of this fusion to the original filtrate it was separately evaporated twice for silica, the first filtrate also, whereby a greater loss of silica was incurred than if the combined solutions had been treated together.

Nos. 7 and 8.—These chemists, attached to the same works, did not ignite the slurry, but dissolved directly in acid and fused the residue with alkali carbonate. Under ordinary circumstances this procedure should not have caused trouble, but the slurry contained considerable organic matter, soluble in acid, which may have affected the subsequent precipitation of iron and aluminum to a marked degree. It is quite impossible to account in this way for the extraordinary values reported for silica, or for the excessive percentages for lime and magnesia, which characterize both slurry and cement analyses by these chemists, and for alumina in their cement analyses. Especially impossible are the figures given for magnesia in the cement. The fact also that two chemists following the same procedure should be able to find 1.14 and 2.03 per cent. of Fe_2O_3, respectively, speaks for itself. Either the grossest incompetence marks these analyses or the reagents used were of phenomenally bad quality. The glassware can hardly be more at fault than in the other analyses, for it is asserted to be Bohemian and furnished by a well-known New York firm. The analyses are therefore excluded, not only in the case of the slurry but of the cement also, as unworthy of serious discussion.

No. 9.—Portions of this analysis are rejected for the same reason as 7 and 8, that is, the manner of effecting solution of the slurry. The iron determination, being made on a separate portion and possibly after solution in a different manner, is not excluded. The cement analysis of this chemist shows normal character, notwithstanding certain deviations from the committee's rules.

No. 19.—The residue from incomplete conversion of the slurry to a soluble state by ignition was fused with sodium carbonate and analyzed separately, not being united with the first filtrate. This introduced uncertainties in the subsequent determinations, the reality of which is sufficiently apparent from a comparison of the values for silica and alumina with those of the standard, and hence justifies exclusion in part.

In individual determinations, a few of the other analyses show lapses from proper care quite comparable with those of 7 and 8, as, for instance, the silica values of 14 and the iron values of 13 in both slurry and cement, and of 11 in the slurry, but the data afforded by the chemists as to the methods used and the internal evidence of the analyses themselves do not furnish sufficient grounds for exclusion wholly or even in great part. Wide variations of the alumina values from the standard are not taken account of when it is plain that this is the result of an erroneous iron determination.

Were space available, it would be of interest before discussing the foregoing analyses to reproduce certain tables and attendant comments of the full report, showing the results obtained by myself when closely following the committee's procedure (using platinum vessels), and also the effect of completing the analyses, after separation of silica, in glassware of different makes. The tables referred to also show not only the percentages derived from the first crude weights, but also those found by applying the corrections usual in exact analysis. It must suffice to summarize the net results.

(1) That with pure reagents and only ordinarily careful work no such variations should be possible as are shown by Tables II and III, even when glassware of good quality is employed instead of platinum. Analyses of the cement made in glass gave: SiO_2, 22.08, 22.10, 22.11, 22.02, 22.30, 22.04; Al_2O_3, Fe_2O_3, 8.39, 8.43, 8.39, 8.22, 8.41, 8.37; CaO, 63.18, 63.03, 63.01, 63.18, 63.17; MgO, 1.16, 1.21, 1.12.

(2) That the solubility of glassware should not make itself so apparent by an abnormally high magnesia result as might seem to be the case in certain of the analyses of Tables II and III, for in all the analyses of the omitted list silica was in solution—up to 8 mg.—but, in agreement with all my previous experience, it is precipitated but little, if at all, with the magnesium phosphate. It seems, therefore, probable that the very high magnesia results in the other cases may have been due to magnesium salts in the water used, as well as in No. 2.

(3) That with cements so completely soluble in acids as the present one, the correction of the silica by hydrofluoric acid and of the alumina by bisulphate ought to be for technical work, certainly for factory control, unnecessary, since they so nearly bal-

ance one another. Any one of my analyses made in glass would serve quite well for all practical purposes, but unfortunately very few of the analyses in Tables II and III conform throughout to the standard anywhere near so well. There is evidently something wrong with the manipulations or the reagents used by the several chemists, as a consequence of which few are able to secure results as good as the least satisfactory of those in the omitted table. They evidently do not work as I do, and, moreover, they do not work alike among themselves. The personal factor seems to be an important one.

(4) That while it might be safe under the conditions assumed above to neglect the corrections on silca and alumina (as was done by analyst 12), it is not safe to apply one and neglect the other. This the following illustration will make clear: The uncorrected values for SiO_2 and Al_2O_3 were 22.12 and 8.59, which became 22.00 and 8.71 when correction was applied to the former only; but the latter held 0.30 SiO_2, so that the true values were 22.30 and 8.41. The wholly uncorrected figures were nearer right than when but half corrected.

DETAILED DISCUSSION OF ANALYSES OF TABLES II AND III.

It is now in order to look at the analyses in greater detail, and because the determinations of silica and alumina are so closely connected, I will discuss under one heading the figures given for silica and the precipitate produced by ammonia.

Silica and the Alumina Precipitate.—The cause mentioned just above, namely, the application of the correction on the silica for alumina and not on the alumina for its contaminating silica, accounts for the chief discrepancies in Tables II and III after excluding the "rejected" values enumerated on pages 1188-1189. This is shown by the following tabulations, where Table IV*a* contains the analyses in which the double correction was made, while IV*b* shows those in which the correction was made only on the silica. The silica was blasted in all cases.

TABLE IV*a*.—SHOWING ANALYSES IN WHICH THE CRUDE SILICA AND ALUMINA WERE BOTH CORRECTED.

	Slurry.		Cement.	
No.	SiO_2.	$Al_2O_3Fe_2O_3$.	SiO_2.	$Al_2O_3Fe_2O_3$.
3	13.95[1]	4.97	22.10	8.72
4*a*	13.78	4.94	21.70	8.60
10*a*	13.39	5.22	21.86	8.83
11	13.20	5.98	22.27	8.83
17	13.38	5.14	22.24	8.36

[1] No hydrofluoric acid correction.

TABLE IV*b*.—SHOWING ANALYSES IN WHICH CRUDE SILICA BUT NOT THE CRUDE ALUMINA WAS CORRECTED.

No.	Slurry. SiO_2.	Slurry. $Al_2O_3Fe_2O_3$.	Cement. SiO_2.	Cement. $Al_2O_3Fe_2O_3$.
1	....	...	22.29	9.68
5	12.62	5.32	21.20	9.04
13	12.88[1]	5.02	21.88	9.18
14	12.10	5.10	20.50	8.41
15	13.55[2]	5.02	22.44[2]	8.62
16	....	...	22.18[1]	8.52
18	12.61	5.53	22.58	9.08

In the first of the above tables, the four silica values for slurry, due to double correction, all fall within the limits 13.20 and 13.78, the standard being 13.51. Analysis 3 is included in this series, notwithstanding the omission of the hydrofluoric acid correction, because it is plain that with the correction made it would occupy an even more favorable place than it does with respect to silica.

The second table contains four of the eight markedly low silica results reported for the slurry— that is, below 13 per cent.— while only one is above 13 per cent. In this, the evaporation for silica was made in glass, while in the other cases porcelain was used, except platinum for the slurry in 13. The other four returns below 13 per cent., namely 1, 6, 9 and 16, are excluded from consideration for the reasons given on pages 1188-1189.

With respect to the silica values for the slurry in Table IV*b*, it seems singular that with such a low general average of uncorrected alumina for the five, the silica should not be much higher than it is. Assuming that the alumina is all accounted for in the values given, there must have been a marked loss of silica in four of the five analyses. Were the alumina considerably higher, the same cause might be assigned that was sufficient to exclude slurries Nos. 1 and 16 from the comparisons, but there is nothing in the data furnished by the chemists who made these analyses that throws any light upon this point. Were it not for the fact that similar deficiencies do not appear in their cement analyses, it might be thought that in some of the cases silica had adhered so tenaciously to the porcelain dish on evaporation as to escape complete removal. This is a cause of error quite likely to arise at times when using porcelain, because of the difficulty of seeing the adhering silica against the white surface. Analyst 16, who evaporated for silica twice in platinum, remarks that the glass

[1] In platinum. [2] In glass.

used for subsequent operations was "easily attacked," which might account, in part, for his abnormal alumina in the slurry, were it not that for the cement it is nearly normal.

Notwithstanding that the results of Table IV*a* are, on the whole, most emphatically favorable to the appliction of the double correction, the fact remains that the general average of the alumina is still far in excess of the standard. This may be in part because the silica correction, as made by bisulphate, does not give the true correction, as I showed conclusively in my paper "Common Errors in the Determination of Silica,"[1] since a large, or even a major, portion of the silica contaminating the alumina goes into solution and can only be recovered by evaporating the dissolved product of fusion with excess of sulphuric acid, and heating till fumes of the acid are copiously evolved. Upon cooling, diluting, and digesting for a time, the whole of the silica collects in flocks and can be readily separated and determined. See, also, page 1205.

In all cases where alumina was twice precipitated (and this was done by all but 3 and 15), except under the conditions of treating the slurry followed by analyst 1, there is no reason to suppose that the high results for alumina are due to coprecipitation of calcium, even when the ammonia used contained carbonate and the liquid, during precipitation, was exposed to gases from the flame beneath. Therefore the variations in the lime and magnesia must be due, in the great majority of cases, to causes quite unconnected with the manner of getting the slurry and cement into solution and with the determining of the silica and alumina, except in the case of slurry No. 1, already alluded to, and possibly one or two others. This it would be impossible to assume, had but a single precipitation of alumina been made, for most chemists do find a little lime with the latter when they take the trouble to look for it, although of the present company 3 and 15, the only ones who tried it, seem to have made a good single separation, as Mr. Blount claims can always be done by the use of a sufficient amount of ammonium chloride. I must admit that a single trial, by myself, on the cement gave a result in accord with his statement, but then I use redistilled ammonia, which is almost free from carbonate, while that coming from the dealers contains a good deal at times and may thereby give rise to rather serious error.

[1] This Journal, **24**, 362.

The excessive value obtained by No. 1 for $Al_2O_3 + Fe_2O_3$ in the slurry has been shown to be due, in part, to the possible counting of considerable calcium sulphate and a little magnesia as alumina, but since an almost equal excess occurs in his cement analysis without the possibility of a similar cause acting, the explanation must lie, in part, in the application of too low a heat. If the alumina was heated with uncovered crucible, as seems to be this chemist's practice, the error may be accounted for.

To sum up the situation as regards silica by a review of all the data, regardless of just grounds for excluding some, it appears that there has been a decided elevation in the average. It is nearly that of the standard in the slurry (13.43 : 13.51) as against 14.37 to 15.18 of the 1901 series, showing an average deficiency of only 0.08 per cent. now, as against 0.81 then. In the cement there appears now an average excess of 0.10 per cent. (22.03 : 21.93), as against a deficiency of 0.81 in 1901 (20.50 : 21.31). It is thus apparent that, whereas two years ago the average error of a large number of chemists was a serious minus one, it is now, in both cases, practically wiped out. The variations from the truth are as likely to be found on one side as the other, though the extremes are as far apart as ever. This last would be a more discouraging feature than it is but for the fact that the returns from analyses 7, 8, 9, 14 and 19 are so abnormal on the slurry as to occupy a position by themselves. Excluding their results, the extreme differences show a marked improvement also, being for the slurry only 1.34 now, as against 2.97 in 1901, and for the cement (excluding here only 14 as utterly abnormal) 1.18 against 2.38.

A similar comparison of the precipitates by ammonia shows the following results: The general average for the slurry is now 0.35 in excess of the standard (5.28 : 4.93) as against an excess of 0.84 in 1901 (7.93 : 7.09), and for the cement 0.52 in excess (8.86 : 8.34) as against 0.90 (10.33 : 9.43) in 1901. The real showing is doubtless somewhat less favorable than it appears from the above, because the alumina precipitates are now smaller than in the earlier series of analyses, but there is nevertheless a manifest improvement.

Iron.—In the foregoing the ammonia precipitate has, for brevity's sake, been spoken of as alumina. The values for the latter constituent, being in all cases determined by difference, are,

of course, affected by any error attaching to the iron. As stated earlier, gross carelessness must have characterized some of the iron determinations. The gravimetric determinations (3 and 19), after separation from alumina by potassium hydroxide, were wide of the standard, as may be seen by reference to Tables II and III, but not to the same degree as some of those made volumetrically. It is of interest to know that the hydrogen sulphide method of reducing iron has given decidedly better results than reduction by hydrogen, though there is still room for improvement by those using the former method.

Aside from carelessness in one way or another, it seems probable that a not unimportant factor in some of the errors is the strength of volumetric solution used. In most cases it was too strong for safety in rapid work on low iron percentages, being from 0.0055 to 0.0105 Fe per cubic centimeter.

Lime.—Except as before mentioned for slurries 1 and 16, the determinations of lime seem to be unaffected by any of the variations from the committee's directions for the solution of the slurry and cement, and there are no data to throw light on the cause of the wide variations, not only from the standard, but among themselves as well. The errors due to solvent action on the glass beakers should affect chiefly the silica and lime, and a portion of all the plus errors in these determinations are to be ascribed to this source. But, as my own analyses made in glass go to show, the errors resulting herefrom are not great enough to account for the large variations reported, unless the glass is much poorer than any that was at my disposal. Neither does there seem to be any decided advantage in the gravimetric method for lime over the volumetric one involving the use of permanganate, except in the case of the cement, where the maximum difference is 1.35 in eleven determinations as CaO against 2.29 by permanganate. If, however, the grossly inaccurate analyses of 7 and 8 are excluded from consideration here as before, the advantage is found to lie slightly with the volumetric method for both slurry and cement, leaving out of account the discrepancy in numbers.

There is internal evidence in a few of the analyses that insufficient heat was employed to convert the oxalate wholly to oxide. For instance, 17 shows in all respects, except lime, a close agree-

ment with the standard, whereas in lime his results are far above the average on both slurry and cement. The last statement holds for 19 too, though the agreement with the standard is not otherwise good. No. 11, on the other hand, shows a marked loss in both cases, with especially high alumina in the slurry, which seems to be indicative of incomplete separation from the latter, notwithstanding that the separation was made twice.

With respect to the temperature required for the complete conversion of calcium oxalate to oxide, it will be well to introduce here a few remarks and an experiment to dispel the common impression that this is a difficult matter. Analyst 1 blasts for an hour or more, but when it is learned that this is done with crucible uncovered, the reason is apparent, especially if the blast is not a powerful one. The following test, made by myself, shows what may be accomplished over a good Bunsen burner only.

A crucible containing 2.9997 grams precipitated $CaCO_3$ weighed 24.4033 grams. The covered crucible was heated for several periods with the results that follow:

	Grams.
Weight after twenty minutes over burner.....	23.1628
Weight after further twenty minutes over burner.....	23.0817
Weight after further twenty minutes over burner.....	23.0801
Weight after inclined blast for twenty minutes.....	23.0790

The total loss was 44.12 per cent., instead of the 43.95 called for by theory, the slight excess being doubtless ascribable to hygroscopic moisture. It is seen that forty minutes' heating over the burner sufficed to effect almost the whole of this with 3 grams of calcium carbonate. For the amounts usually encountered in analysis, of which cements afford about the maximum, ten minutes' heat of the Bunsen burner is almost as effective as an additional five minutes' blasting, which latter is usually ample. Could the Bunsen heat be applied effectively with exclusion of the flame gases from the interior of the crucible, the blast would be quite unnecessary at the end. It is, however, assumed that the crucible rests in a triangle of platinum and not of clay. It is also my custom to use an inclined blast on almost all occasions requiring this mode of heat application, and usually without allowing the flame to envelop the lid of the crucible. Hereby flame gases are largely or altogether excluded, and, consequently, in the case of

cements and limestones, given an equal temperature, more rapid loss of their carbon dioxide results than is possible with a vertical blast.

One possible cause of error in the lime results remains to be mentioned. Unless the lime is weighed soon after ignition—say not later than half an hour—the result may be too high. It is not known to what extent, if at all, this error affects the results under discussion.

Magnesia.—Regarding the discrepancies in magnesia there is little that can be said. When averages for 1901 and 1902 are compared, the present are found to be even a little worse than the earlier ones, and that too with smaller amounts of magnesia to deal with. Even allowing for considerable solvent action of reagents on the glass, it is difficult to see how this should give rise to such extraordinary results as some analysts report. It seems not impossible that the abnormally high magnesia returns were, in all cases, due to impure water, as was found to be the case with those of analyst 2. Even where the ammonium salts have been removed by nitric acid (method of J. Lawrence Smith), as recommended by Mr. Blount, the results are still high, as in both analyses 19.

The influence of impurities in stock solutions is one that should not be lost sight of. The practice of using stock solutions of such reagents as ammonium oxalate and sodium phosphate is dangerous, unless the solutions are renewed at frequent intervals. It is my practice to use the solid salt and dissolve it as wanted.

Sulphur.—For all but No. 3, the figures for sulphur trioxide represent only the sulphate sulphur. No. 3 reports only total sulphur. The only point calling for special comment is the comparison of the results as they were obtained with or without removal of silica by evaporation before adding barium chloride. Even excluding the particularly abnormal results of 14, the advantage is still with those who do not remove silica (5, 6, 9, 10*a*, 12, 17), although the comparison is not altogether satisfactory, because of the difference in the numbers using the two procedures. I am inclined to ascribe the higher values in the one case largely to absorption of sulphuric acid during evaporation for removal of silica, especially where water-baths heated by gas were used. That this source of error is a very real one has been long since shown. Impure water may be a factor in other cases for the

deviations in excess of the standard recorded by both procedures. The high value reported by No. 2, in his original analysis, is known to have its origin in the above source, and it may very well be, in view of the poor quality of the water reported subsequently by others, that this explanation fits other cases. That Stoddart should have found[1] frequently more sulphur in coals when not separating silica than when doing so, is contrary to all my experience in silicate work, where duplicates agree usually exactly, and, if they differ, are as likely to be high by one way as by the other.

Ignition Loss.—The results for loss on ignition will not be discussed in detail because the experiments, referred to below, have shown clearly enough why the results vary, and must vary, unless a closely defined method for determining this loss is followed. Such precision is not to be found in the committee's directions for the determination of this factor; hence, no blame can attach to those who obtain results varying from the standard. Several of the chemists stated that in their results "loss on ignition" comprised not only water and carbon dioxide, but also more or less sulphur trioxide, depending on the temperature of the blast, besides organic matter and possibly one or two minor factors. In my own analyses, it was supposed to include all possible factors except loss of sulphur from either sulphates or sulphides, for, unless the heat passes a certain point, the sulphides are oxidized to sulphates and no sulphur is lost, being retained by the lime. This is the explanation asked for by Mr. Blount in his reply[2] to certain remarks of mine at the foot of page 1221.

Mr. Blount is perfectly justified in objecting to the blast for "loss on ignition" in cements and cement mixtures containing sulphur when applied in the manner prescribed by the committee, but, as described below, the method is accurate for all reasonable demands, and results agreeing within 0.1 or 0.2 per cent. can be obtained almost as often as desired. It happened that, without special study of the subject, I had employed the right conditions from the start, but Mr. Blount's inquiry led me to take up the matter in some detail, and the results I now communicate.

It may be said at once that the variations in "loss" are not attributable to absorption of carbon dioxide and water from the air, unless there was great lack of care, and even then this can be

[1] This Journal, **24**, 852.

[2] *J. Soc. Chem. Ind.*, **21**, 1223.

but a minor cause, as the data given on page 1183 show. Hence, my own former doubts and those of S. F. Peckham[1] on this point were largely unfounded.

Trials in great number were made on both slurry and cement under varying conditions. It was found, as above said, that the sulphides could be easily and quickly oxidized without any loss of sulphur and yet with complete removal of water, carbon dioxide, and organic matter. The proof of this was repeatedly obtained by finding in the ignited product as sulphate soluble in hydrochloric acid exactly all the sulphur that the cement or mixture originally held in both sulphate and sulphide condition. Such a complete change can be effected in a short time and without any need to be very cautious in applying the heat. It may be turned on nearly full at the start.

In all my experiments, ignitions were effected in covered platinum crucibles of about 20 grams weight. Chemist No. 1 followed the practice recommended by me of fitting the crucible in a hole in asbestos board, but removed the cover, and in this last fact lies the explanation of the excessive time required by him for securing constant weight, and the too low results when obtained. My experiments show that even without the protection afforded by the asbestos board there need be no great error with an inclined blast if only the precaution is taken not to let the flame envelop the whole crucible, but only to impinge strongly against the lower third. In using asbestos board, particles tend to cling to the crucible and to remain attached when the latter is removed after ignition; hence, I prefer, as much cleaner and no more expensive in the end (for the same asbestos serves but a few times), a sheet-platinum disk with a hole for the crucible, the disk in its turn covering a larger hole in asbestos board. A further advantage of this modification is that, because of the higher heat obtained than when the crucible is in contact with asbestos, the duration of the heating is shortened. A muffle answers equally well, as claimed by Mr. Blount (for time required see page 1207).

I have assumed that the loss shown when none of the sulphur has as yet been expelled is to be taken as correct, since in no case was there the slightest effervescence on dissolving in hydrochloric acid, nor any trace of organic matter left. That this assumption is entirely justified was shown by the close agreement

[1] *J. Soc. Chem. Ind.*, **21**, 831.

(in case of the cement, for which alone could the calculation be made) of this value with that obtained as the algebraic sum of all factors entering into the loss. A similar agreement appeared in my discussion of the 1901 series of analyses. But, because of the unavoidable variations in the heat supply used by different chemists, each one should ascertain, once for all, the effectiveness of his burner, blast, or muffle, by ascertaining, as I did, the limit of time beyond which sulphur begins to be volatilized, as shown by the ignited "mix" or cement yielding less total sulphur than before ignition. This necessarily, however, involves rather more accurate determinations of sulphur than most of those reported either now or in 1901.

The temperature at which carbon dioxide escapes from calcium carbonate being so much lower than that causing dissociation of the sulphate, is the reason why comparatively brief application of heat under the above conditions effects complete loss of carbon dioxide and little or none of sulphur trioxide. But it is not the above mode of ignition that must be used to convert the slurry to a wholly soluble cement. No disk protection is then allowable.

It is apparent from my experiments that most chemists employed far too protracted ignition in determining "loss," and that in extreme cases all, or nearly all, the sulphur trioxide was included in the loss. But in many cases there was a further factor making itself felt, for long before the last of the sulphur trioxide is expelled alkali begins to volatilize, and it is easy to remove all, or nearly all, in this manner. The alkali is volatilized as oxide and may be collected in quantity on the under side of the crucible lid. At the intense temperature of the rotary cement furnace this action must play an important part, and to it is to be attributed the great loss of alkali, noted by me in the cement of 1901, as compared with the raw "mix" from which it was made, an observation which is repeated in the present case and must be general in cement burning.

PROPOSED MODIFICATIONS IN THE COMMITTEE'S DIRECTIONS FOR THE ANALYSIS OF CEMENTS.

From the foregoing it is apparent that the committee's method of procedure has, in many respects, not been subjected to a fair or exhaustive trial. Furthermore, because of the real uncertainty regarding the quality of much of the water used, the value of this

report is below what it would otherwise be. Nevertheless, certain facts have appeared from my experimental work in the light of which modifications of the committee's directions for the analysis of Portland cements and raw mixtures used in their making are in order. These I will now consider.

Rendering Raw Material Soluble.—The committee's direction, following my own recommendation, to ignite the "mix" at an intense heat in order to render it soluble in hydrochloric acid, are thoroughly sound in principle and in accord with the practice of Messrs. Stanger and Blount. By doing this, the material undecomposed by the acid should, in no case, probably, exceed 0.1 per cent. of the sample, and it is sometimes much less. By this it is not meant that no insoluble matter appears other than undecomposed silicates, for a little silica is always separated in a flocculent, non-gelatinous, easily filterable state. The unattacked particles can always be detected by their gritty character when touched with a rod.

Under no circumstances may a large residue of undecomposed matter, found at this stage, be evaporated with the solution to dryness and treated as if it were silica (as two or three chemists have done in the present series of analyses), for it may, and probably does, contain lime in addition to alumina, ferric iron, etc. The error in silica and alumina, caused by this lime being weighed as sulphate, after the hydrofluoric acid correction, has been discussed on page 1188.

The point has been raised that the strongly ignited material dissolves very slowly, being dense and semifused. If, however, the lumps are gently pressed upon with the flattened tip of a rod from the moment the acid strikes them, solution becomes a matter of no difficulty at all. In spite of the ease with which this conversion to a soluble state can be reached in fifteen or twenty minutes, quite a number of chemists failed by lack of blast of sufficient intensity. The committee recommends in such cases to filter off any undissolved matter, to ignite, to fuse it with sodium carbonate, and to add its hydrochloric acid solution to the main filtrate. Had these directions been followed in certain cases, fewer analyses would have been thrown out of court.

In order to obviate the need for a filtration and fusion of a possible residue, one chemist, W. R. Oglesby, recommends to strongly ignite a mixture of the material with only enough sodium

carbonate to cause sintering. It is claimed that solution in hydrochloric acid is then complete, that the amount of alkali introduced is so slight as to give rise to no appreciable error in subsequent operations, and that the necessity for correcting silica by hydrofluoric acid is avoided. My own tests show that the first claim is well grounded when even so little as 0.5 gram of the flux to 1 of "mix" is employed. But the reason for the third is not obvious, for it has never been my fortune to see silica separated by evaporation from a solution containing aluminum, iron, titanium, and phosphorus, or even the first of these alone, which was so pure that no contamination was revealed by the hydrofluoric acid treatment. The residue is rarely under 1 mg. and may be twenty to thirty times that amount in special cases (not cements). My own limited experience with cements shows that it runs from 1 to 2 mg. after a single evaporation for silica and slightly more after a double one. Still, no strong objection can be brought against this method of attack of the raw mixture on the score of accuracy, and if it on a general trial should meet with the approval of cement chemists, there may be no objection to its superseding the blast ignition without addition of flux. But the amount of this flux should be rigidly kept down to the lowest limit, not exceeding that given above.

Determination of Inert Constituents in Cement.—Mr. Oglesby would also apply the above mode of attack to cements as well, but this brings up the question whether the committee shall see fit to take account of the existence of cements containing acid-soluble constituents in appreciable amount. These undoubtedly do exist here, as well as abroad, and it seems reasonable and proper that inert constituents, when present, should be reported as such and not help to swell the active components. But if the determination of these inert constituents is to be made, I cannot recommend that the directions of Messrs. Stanger and Blount be followed, for the reasons set forth in my criticism of certain features of their paper,[1] but must adhere to the procedure there outlined by myself. I do not agree with their statement that no foreign matter is to be found with the silica separated from cements, nor, do I think, will many others do so who look carefully into the matter (see remarks relating to this point a few paragraphs above, page 1201).

[1] *J. Soc. Chem. Ind.*, **21**, 1222.

Solution of Cement and Ignited "Mix."—The committee's directions for dissolving cements and ignited cement mixtures may very well be modified in the interest of time-saving by adopting the practice of Messrs. Stanger and Blount,[1] for to digest, and especially to dilute strongly, before evaporating causes quite unnecessary delay. Usually, in two or three minutes after pouring the acid upon the moistened cement, solution is effected and evaporation may begin.

Dehydration of Silica.—Messrs. Stanger and Blount's plan of baking on a hot plate, at a temperature of about 200°, is a very speedy way of rendering nearly all the silica insoluble and saves much time. It may be unhesitatingly recommended for a first evaporation. But at this point my approval of their procedure ceases. I can refer only to my experiments quoted on page 1221[2] in refutation of the claim that a single evaporation for silica suffices by their procedure. Their later results (p. 1223) only serve to confirm my objections instead of overturning them. If an error of over 0.2 per cent. in the alumina is negligible, then why do the authors regard it necessary to reject, as unfit for use, filter-paper which would introduce into an analysis an error of less than one-tenth of the above? But, in addition, the authors do not give us their way of analyzing the precipitates of Al_2O_3 and Fe_2O_3 in order to show that the amounts of silica they give were all that these precipitates contained. If it were done by solution of the Al_2O_3 and Fe_2O_3 in an alkali bisulphate, they obtained but a minor portion probably of the total silica. As I have shown elsewhere,[3] that method, as hitherto carried out, gives utterly fallacious results, and it is only by the exercise of a certain precaution that all silica can be recovered. Even after two evaporations, the iron-alumina precipitate contains usually from 1 to 3 mg. of silica. Nor is this silica "more likely to be due to dust and outside impurities than to residual silica in the cement itself,"[4] if the water and reagents were pure.

No change should therefore be made in respect to the double evaporation and filtration for silica. It is not important, except

[1] *J. Soc. Chem. Ind.*, **21**, 1217.
[2] *Loc. cit.*
[3] This Journal, **24**, 362.
[4] *J. Soc. Chem. Ind.*, **21**, 1223.

as a matter of time-saving, whether the heating of the separated silica be done at steam-bath temperature or at that of the hot plate.

Alumina, Iron Oxide, Lime, Magnesia.—I do not feel that any fundamental changes in the directions given by the committee for the determination of these constituents are called for either by the comments of different writers or by the testimony of the analyses themselves. The amount of bisulphate to be used for the solution of the ignited alumina, etc., should be reduced from 10 grams to 2 or 3. Care should be taken to make a blank experiment with the reagent to ascertain its silica contents, if it has any.

I agree with Messrs. Stanger and Blount that quite satisfactory separations *can* be made in cements and cement mixtures, of alumina and iron from lime, and of lime from magnesia, by one precipitation, separations which would satisfy all requirements of the cement trade, and I have made them myself. But this can only be accomplished by the employment of really good reagents and utensils. With the ammonia used by nearly every one, varying perhaps in quality originally, not redistilled over lime, and contaminated from the glass bottles, it is hardly possible that accurate results can be obtained by single precipitations. Probably most ammonia used contains carbonate. I have found this to be so with that which we buy as of good quality. Hence, unless carefully redistilled over lime, the aluminum and iron oxides must be contaminated by calcium carbonate. Mr. S. S. Voorhees, of the supervising architect's office of the United States Treasury, finds this contamination to be less than 0.25 per cent., but it may often be more in careless work, and it is to avoid the effect of variable errors like this that I would make double precipitations the rule.

In the numerous analyses made by myself for this report, I have thoroughly tested the time-limit for the settling of calcium oxalate after precipitation, and find that very little, indeed, is gained by allowing to stand for more than twenty minutes after removal from the source of heat. The lime in the first filtrate will hardly ever exceed 1 mg. when the quantities to be precipitated are so great as in limestones and cements.

In blasting lime, the crucible should be always covered, and it is advisable that the blast-flame impinge only against the lower part of the crucible, at an angle of about 45°. The flame should not envelop the lid of the crucible, because when it does the contents are ever in an atmosphere of carbon dioxide, and the complete reduction to oxide is retarded. The heat of a good blast-lamp is, however, so many hundred degrees above the temperature of decomposition of calcium carbonate that no difficulty need be experienced in getting an unchanging weight, even if this precaution is not observed. With it, however, no ignition should ever require over ten minutes, and a second heating is, indeed, rarely made by myself.

I now regard it as quite unnecessary to blast the relatively small amounts of magnesium pyrophosphate obtained in cement analysis. Indeed, if blast heat is prolonged beyond two or three minutes, loss may ensue. This is especially so, if the phosphate, after blasting, shows signs of fusion.

If the double precipitation of magnesium is to be retained, I do not deem it at all essential that the procedure given by the committee be followed. That procedure, of Wolcott Gibbs, is designed to give a precipitate of normal composition, but if a second precipitation is to follow, it is immaterial whether the first is of normal composition or not, so long as all is precipitated. Therefore, it does not seem logical to boil with the precipitant in an acid solution before rendering ammoniacal, when the object can be more simply attained. The amount of precipitant should be largely reduced if a single precipitation only is intended, and it is unnecessarily large, in any case.

Application of Corrections to the Foregoing Determinations.—With good work, little is gained in analyzing cements by correcting the ignited silica and alumina for the contaminations which they invariably contain, provided two evaporations and filtrations have been made for silica. It is also shown on page 1191, however, that the one correction should not be made without the other, for then the errors on the alumina may be large, especially where, as is most always the case, glass vessels are used for the precipitations.

The bisulphate correction for silica in the alumina must be made, not in the usual way, but, in order to avoid serious error, as follows: The bisulphate fusion is to be dissolved in water to which a good deal of sulphuric acid is added, and then evaporated

in platinum and heated till acid fumes are copiously given off. When cool, the pasty mass is redissolved in water, digested till all but the flocculent silica is in solution, then filtered. The ignited and weighed silica is to be checked by hydrofluoric and sulphuric acids, like the main silica.

I have recently followed J. Lawrence Smith's strong recommendation to use the sodium acid-sulphate for this purpose instead of the potassium salt, and with very good results. There is then no difficultly soluble potassium-aluminum sulphate to dissolve before filtering off the silica, but solution is speedy, and, furthermore, the action of the sodium salt on the ignited iron-aluminum oxides is more energetic, so that much time is saved by its use. There is, however, the disadvantage that the salt is far more difficult to keep in fusion than the potassium salt, so that the progress of solution of the oxides on the bottom of the crucible cannot be so well followed.

Sulphur.—Notwithstanding some adverse testimony from another source than the chemists who have participated in these series of analyses, I am fully of the opinion that the practice of not first removing silica where small quantities of sulphur are in question is perfectly safe. The only condition is that the silica must not be allowed to gelatinize, and this I never have the slightest difficulty in maintaining, first by using not very strong acid for effecting solution and then by diluting freely as soon as solution is accomplished. The vessel may then be placed on the steam-bath or even boiled on the iron plate without fear of gelatinization resulting. This mode of procedure avoids the contamination by sulphuric acid from the flame of a water-bath that is heated by gas, which is certain to result if the silica is first dehydrated in the usual way. When an oxidizing fusion of the cement or mixture is made, the asbestos or platinum-asbestos protection, mentioned in the paragraph below, should be used.

Ignition Loss.—Instead of igniting over a free blast-flame, the covered platinum crucible should be inserted about two-thirds of its depth into a close-fitting hole in asbestos board, or, better, in a disk of platinum foil which itself covers a large hole in asbestos board. The flame should strike at an angle of about 45°, and, when using the disk, for thirty minutes with 1 gram of slurry or limestone mixture, and five to ten minutes with a cement. Even

with only a good Bunsen lamp (using the disk) practically the same result can be reached in sixty minutes on a slurry or limestone and in thirty minutes on a cement. With a hot, closed muffle, ten minutes' time suffices with either raw mixture or cement, the crucible being placed about two inches from the door.

But each chemist should ascertain for himself, by direct experiment, what his blast or muffle can do, and this he can best learn by experimenting with a standard material whose composition is known. It would be, in my opinion, of great advantage to all cement chemists if the committee would see to the preparation of a large sample of limestone mixture, sufficiently large to last for many years, which could be issued to all applying for it. I select limestone instead of slurry or cement on account of its unchangeability under varying atmospheric conditions.

CONCLUDING RECOMMENDATIONS.

Probably the most fruitful plan for arriving at a method of procedure that would best suit the conditions prevailing in the majority of cement works would be through a subcommittee or a new committee of not more than three well-selected members, who should not only be analytical chemists, but men familiar with cement works. Now that the conditions governing accurate work are understood, such a committee should be able, by actual experiment on a standard sample like that mentioned above, to work out a detailed scheme of analysis that would be a satisfactory compromise between the imperative demands of the factory for immediate results, on the one hand, and a proper regard for reasonable accuracy on the other. Such a method might be known as the "factory control method," while for more precise work one of greater refinement might be given in detail and its employment strongly recommended, if not prescribed. While I agree, in general, with Messrs. Stanger and Blount in thinking that the consulting chemist, at least, should be untrammeled in the choice of his methods, it is, nevertheless, unfortunately true that no general analytical chemist is or can be equally familiar with all lines of work, nor are all of equal judgment in the selection of methods. Men of skill and judgment can often arrive at like results by diverse routes, but it is certain that this is not yet so with respect to all of the stages of a silicate analysis, even so simple a one as that of cement, and till this condition is

reached I think it were well to prescribe the procedure at certain stages.

But, after all, no amount of careful attention to any analytical process is of much avail unless the materials used are of good quality. Too many chemists, as appears from the replies furnished in the present case, assume, without positive knowledge, that those used by them are satisfactory; others report one or the other as of good quality without giving any quantitative data in support of such an assertion. No chemist can be said to do justice to his employers or patrons who does not *know* what order of error his results may include, arising from impurities in reagents and the solvent action of those reagents on his utensils, or from other causes either preventable or admitting of exact correction. Too often, beyond doubt, is a known contamination thoughtlessly excluded as negligible when, in fact, a quantitative test might have shown the falsity of the belief.

FOURTH SESSION OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS.

HELD IN BERLIN, GERMANY, JUNE 4, 1903.

Received September 22, 1903.

The following were present:

Professor Dr. A. Herzfeld, chairman.

Privy councilor, Prof. Dr. Landolt, Berlin.

Baron von Donner, chairman of the *Verein der am Zuckerhandel betheiligten Firmen,* Hamburg.

Privy Councilor Koenig, chairman of the board of directors of the *Verein der Deutschen Zuckerindustrie,* Berlin.

Professor Dr. Brodhun, representative of the *Physikalisch-Technische Reichsanstalt,* Berlin.

Professor Dr. Schoenrock, *idem,* Berlin.

Privy Councilor Professor Dr. von Buchka, delegate of the *Kaiserliche Reichsschatzamt,* Berlin.

Government Councilor Weinstein, representative of the *Kaiserliche Normal Aichungsamt,* Berlin.

Government Councilor F. Strohmer, Vienna, Austria.

J. Ragot, director of the *Syndicat des Fabricants de Sucre de France.*

K. Fischmann, director of the Russian Sugar Manufacturers' Association, Kiev.

Dr. Raschkowitsch, director of the chemical laboratory of the Russian Sugar Manufacturers' Association, Kiev.

François Sachs, representative of the *Société Technique et Chimique de Sucrerie de Belgique,* Brussels.

Dr. F. G. Wiechmann, representative of the American Sugar Refining Company, New York.

E. Silz, representative of the *Association des Chimistes de Sucrerie et de Distillerie de France,* Paris.

A Watt, member of the Beetroot Sugar Association of Lancashire, Liverpool, England.

S. Stein, member of the Beetroot Sugar Association of Lancashire, Liverpool, England.

Also the following members of the Commission:

Dr. C. Ahrens, Hamburg; Lobry de Bruyn, Amsterdam; Professor Dr. Frühling, Braunschweig; Dr. G. Götting, Breslau; Dr. B. Hermann, Hamburg; F. Herles, Prague; Dr. A. Langfurth, Altona; Dr. O. Wendel, Magdeburg; Dr. R. Woy, Breslau, as well as numerous other chemists connected with the sugar industry.

After the opening of the session, the chairman expressed his special thanks to Privy Councilor Landolt, the scientific founder of the polariscopic method, as well as to Baron von Donner, and to Privy Councilor Koenig, for their coming. The chairman then outlined the previous work of the Commission.

He requested Mr François Sachs, of Brussels, and Dr. F. G. Wiechmann, of New York, to again undertake the editing of the French and of the English text of the proceedings.

The sets of quartz-plates which had been selected by the *Physikalisch-Technische Reichsanstalt* in Berlin, and which had been tested in the laboratory of the *Verein der Deutschen Zuckerindustrie* as to their sugar value, have been distributed to proper central stations of the countries interested, and there are kept at the disposal of chemists. These plates have been tested in almost all of the countries which have received the sets, and have been

found correct. Some of these stations have thus far not made a report as to the results of this reexamination, and such a report is, therefore, requested.

Execution of the Paris agreement, according to which chemically pure sugar is to be used for the adjustment of polariscopes and for the testing of plates, has, in some countries, met with difficulties because they could not succeed in preparing chemically pure sugar. The laboratory at Berlin, therefore, offers to furnish chemically pure sugar.

In the determination of invert-sugar, a difficulty has arisen, inasmuch as the English chemists have, of late, again declared against the clarification with basic lead acetate; the Commission will, therefore, have to seek means and methods to prevent, in this respect, loss of uniformity, now secured in the methods of analysis.

THE DAY'S PROCEEDINGS.

(I) "Report concerning practical experiences made with the uniform methods of analysis agreed upon in Paris."

Doctor Hermann delivered an address on this topic; this is published in the *Zeitschrift des Vereins der Deutschen Zuckerindustrie.* The speaker was of the opinion that numerical proofs of the success of the Paris agreement could not be adduced, yet the fact could be stated that the differences have decreased in number. To avoid a warming of the polariscope tubes in handling, he recommended covering the same with rubber.

Privy Councilor Professor Dr. von Buchka made the following statements:

The International Commission for Uniform Methods of Sugar Analysis decided, in the year 1900, that the determination of invert-sugar in raw sugars is to be carried out according to the method of Prof. Dr. A. Herzfeld. It seems desirable to abandon this method and to prepare Fehling's solution in such a manner that the weighed constituents be brought into solution with water, up to one liter. This would be in accordance with the method otherwise customary in the preparation of normal solutions. This method of procedure has, moreover, been adopted in the official directions for the analysis of wine, decreed in Germany in the year 1896. It seems desirable that the manner of preparing Fehling's solution be always the same, whatever purpose the sugar determinations may have to serve.

Professor Dr. Herzfeld replied that Herzfeld's method differs from the method used in the examination of wines, not only in the manner of preparing Fehling's solution, but also in the employment of a definite heating surface. A further essential difference is the fact that the reaction is suddenly interrupted after two minutes by the introduction of cold water. On this account all tables which have been prepared by Meissl and others are of no value, unless one is also willing to return not only to Soxhlet's Fehling's solution, but also to the antiquated working methods for which these tables have been established.

In the determination of invert-sugar, the 10 grams of cane-sugar which are dissolved in Fehling's solution exert a great influence on the amount of copper reduced. It would, therefore, be dangerous to alter the concentration of the solution before this influence shall have been carefully studied, and a decision arrived at as to whether it might not be necessary to establish a new table for the solutions made thus differently.

Mr. Pellet declares himself as opposed to the use of basic lead acetate as a clarifying reagent, and for the heating of the solution to reduce the copper on the water-bath, instead of over the naked flame.

Government Councilor Strohmer believed that he might declare in the name of the Austrian chemists that they agree with the remarks made by Professor Herzfeld, for a change in the manner of preparing Fehling's solution would necessitate a change of tables for the determination of invert-sugar, that is to say, would amount to a change of the method itself. Commerce has adopted Herzfeld's method. Each produce-exchange demands, in the certificate, determinations of invert-sugar according to Herzfeld. If the method were to be changed, the consent of commerce would have to be secured. It was the determination of invert-sugar which held back, for so long, the introduction of uniform methods, and Mr. Strohmer expresses the wish that this agreement, which was so difficult to bring about, may not again be disturbed so soon by the introduction of a new method of preparing Fehling's solution. Dr. Woy next presented an additional report (*ad. 1.*) of the day's program. He, too, is unable to present data which cover all Germany, but in a compilation of Silesian analyses, made in duplicate, he made the observation that series of analyses which

were in excellent agreement were suddenly interrupted by series which exhibited serious differences, and that in such cases the super-analysis also did not tally with the series of the former analyses, but at times represented an accurate average. In such cases only the samples can have been the cause of the differences.

He recommends the collecting of such cases in order to determine, numerically, how often greater differences arise and whether, in such cases, the fault is to be ascribed to the method, the analyst, or the taking of the sample. Furthermore, he desires a more exact definition of the maximum amount of basic lead acetate, and of aluminum hydrate, allowable, in order to exclude, as far as posible, the source of error inherent in the volume of the precipitate.

Dr. Koehler-Maltsch was of the opinion that differences which still occur in polarizations must be ascribed to faulty graduation of the flasks.

The Commission decided to elect a Sub-commission for the elucidation of the questions at issue. This Sub-commission is to consist of Messrs. Watt, Wiechmann and Strohmer, and is to study especially the question of clarification by basic lead acetate, as well as the question of a change in Fehling's solution. Privy Councilor von Buchka promises his assistance in these investigations.

(II) "The valuation of 'Sand' and 'Krystallzucker" in International trade."

Government Councilor Strohmer, of Vienna, discussed this question. His lecture is printed in the *Zeitschrift des Vereins der Deutschen Zuckerindustrie.* The address evoked no discussion.

(III) "Introduction of International uniform directions for sampling raw sugars." Mr. Wiechmann stated that he considered it to be very desirable that a 100 per cent. sample be taken, that is to say, a sample from every package wherever this may prove at all possible. Furthermore, he added that great attention ought to be paid to the manner in which samples are taken, for, otherwise, very peculiar results would be secured, especially with raw sugars of lower grades.

Director S. Stein, Liverpool, explained that in England sugar, on importation, has to pay duty according to polarization. It is of

great importance that for this purpose the same sample be used which is used in effecting the purchase. The English authorities found very marked differences between their analyses and the results which the refineries declared. The cause of this is to be sought in the different manner of sampling the sugar. It is very difficult to obtain a correct average sample, especially of cane-sugar. As is known, cane-sugar is put up in different kinds of packages. For instance, in bags, in mats, in hogsheads, etc. Furthermore, a cane-sugar is not homogeneous, but varies in composition in different parts of the package. Thus, in cane-sugar, syrups and semifluid masses occur. All this has to be taken into consideration. It is necessary that the sampling be done in such a manner that the sample drawn be truly representative of the sugar. Sampling shall be done in such a way that the sample shall be taken from different parts of the package, and at one time. It is well known that stored sugar changes its composition. A sugar which has a certain composition to-day has a different composition one or two months hence. It is also necessary that the sampling be done on a given number of bags or packages. Mr. Stein, therefore, advised the adoption of a resolution or the addressing of a request to the International Commission to consider what points of view should necessarily be borne in mind in order that uniform sampling, especially of cane-sugars, may be achieved. The speaker is confident that the conclusions of such a forum, in this most important matter, would prove binding and elucidating.

At the request of the chairman, Mr. Wiechmann agreed to prepare a compilation of the different directions which are in force in the various countries interested in the sugar industry, and to submit this preliminary report to the Sub-commission, consisting of Messrs. Wiechmann, Watt and Strohmer.

It was the general opinion that it was necessary to consult expert chemists more than has been done heretofore in the drawing-up of working directions for samplers.

(IV) and (V) "Influence of temperature on the specific rotation of sucrose," and "Introduction of temperature-corrections when the temperature of observation differs from the temperature of 20° C., which has been accepted as the normal temperature." These two topics were disposed of together.

Dr. Schoenrock discussed the first-named of these subjects. His address is printed in the *Zeitschrift des Vereins der Deutschen Zuckerindustrie.*

In the discussion of this address, Mr. Wiechmann, while expressing appreciation of Schoenrock's labors, declared against the introduction of corrections to polarizations obtained in actual practice. Professor Herzfeld took the same position, because, besides the variations in specific rotation, still other factors come into play, for instance, the variable amount of evaporation which takes place on filtering the solution.

Professor Brodhun remarked that, if correct corrections are applied, correct results must be obtained. It was decided that the individual members of the Commission, for the present, are to study the question of corrections on their own account.

(VI) "Determinations of the sugar subject to duty or bounty contained in saccharine products and fruit preserves."

In this connection, the chairman read a paper prepared by Mr. H. W. Wiley, of Washington, who, to the regret of those assembled, was prevented from attending. The chairman closed his remarks with the words that the point of view taken by Mr. Wiley would probably meet with the unanimous approval of the Commission. There was no objection to this comment.

(VII) "Chemical control as an aid to the Entrepôt-system sanctioned by the Brussels convention."

The printed address of Professor Herzfeld, on this subject, was in evidence. It also appeared in the *Vereinszeitschrift.* There was no debate on this address.

The following papers, which figured on the program of the Congress of Applied Chemistry, were also disposed of during the session of the Commission.

(1) Lecture of Mr. Wiechmann on "A restant source of error in optical sugar analysis." The question of the influence of the basic lead acetate precipitate, discussed by Mr. Wiechmann, is to be further studied.

(2) Lecture of Mr. Dupont: "Sur l' unification des échelles saccharimétriques et l'adoption d'une échelle á poids normale de 20 grammes."

Mr. Dupont was not present. Decision on his proposition to introduce a normal weight of 20 grams is deferred.

(3) and (4) A paper by Mr. David R. Davoll: "A study in the determination of raffinose," and a paper by the same, "Should raffinose be considered as non-sugar in calculating the quotient of purity?" were presented in print. There was no discussion of these papers.

(5) A lecture by Mr. Sachs: "Shall chemical measuring instruments be graduated according to the old Mohr method, or according to the new official method of France and Germany?" A discussion followed this address. Professor Weinstein and Privy Councilor von Buchka stated their opinion to be that a single section should not adopt a resolution in this matter, and declared a return to Mohr's method a step backwards. Mr. François Sachs disputed the latter assertion.

The meeting then adjourned.

F. G. WIECHMANN, *Secretary.*

NOTE.

On the Emulsifying Action of Soap.—Experiments on the emulsifying power of soap solutions have been recently published by H. W. Hillyer.[1] In these it is shown that the effect is due to the lowering of the interfacial tension at the interface oil-soap solution, caused by the non-hydrolyzed soap contained in the aqueous solution. The variation of interfacial tension with the concentration of the soap solution was quantitatively studied by Hillyer by means of a dropping pipette.

It may be remarked, however, that not only have exactly similar conclusions been arrived at previously by me, but they have been obtained by an almost identical method and pulished in one of the most universally read scientific journals.[2]

Doubtless my paper must have escaped Mr. Hillyer's notice, for in his second paper he refers to himself as a pioneer. In my experiments, drops of a neutral, fatty oil (or of a neutral hydrocarbon oil) containing a specified amount of free aliphatic acid were allowed to ascend through an alkali solution of known strength. My first experiments (not published) were made by

[1] This Journal, **25**, 511, 524 (1903).

[2] *Ztschr. phys. Chem.*, **31**, 42 (1899).

allowing drops of a neutral oil to ascend through an aqueous soap solution, but this method was abandoned in favor of the former one, owing to uncertainty as regards the amount of hydrolysis in the soap solution. If Mr. Hillyer will refer to a recent paper by Krafft,[1] which also seems to have escaped his notice, he will find that a perfectly pure "soap" solution will *not* emulsify a neutral oil. This effect appears to occur only when the soap solution contains an excess of free alkali (or even alkaline chloride). From this it would seem that the lowering of interfacial tension and consequent emulsification are due to the production at the interface of a colloidal layer or membrane.

In conclusion, although Mr. Hillyer's paper forms an interesting contribution to an interesting subject, it is necessary to point out that neither his main conclusion nor the method by which it was obtained, is new.

F. G. DONNAN.

ROYAL COLLEGE OF SCIENCE, IRELAND,
August, 1903.

NEW BOOKS.

CHEMISTRY OF THE DYE-STUFFS. By DR. GEORG VON GEORGIEVICS, Professor of Chemical Technology at the Imperial and Royal State Technical School at Bielitz. Translated from the second German edition by CHARLES SALTER. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1903. vi + 402 pp. Price, $4.50 net.

This book, originally designed to form a section of a text-book on the "Technology of the Textile Fibers," was afterwards modified into a separate volume, chiefly in order to render it more accessible to chemists interested in the chemistry of dye-stuffs rather than in the dyeing and cloth-printing industries. For this reason, all particulars relating to the application of the dye-stuffs are relegated to the author's companion volume—"Chemical Technology of the Textile Fibres."

The aim of the author has been to provide a text-book presenting to the student, in as lucid and condensed a form as possible, the extremely wide domain of the modern chemistry of the dye-stuffs.

[1] *Ztschr. phys. Chem.*, **35**, 371 (1902).

Care has been taken to bring into prominence all the relations known to exist between the various dyes and groups of dyes, as well as the connection between color and constitution, as the proper appreciation of these relations form the main object of the study of the chemistry of the dye-stuffs. An endeavor has also been made to clearly define the true importance attaching to the several dye-stuffs, whether theoretical, practical, or historical.

Owing to the rapid progress made in connection with the dye-stuffs since the appearance of the first edition of this book, the sections dealing with the azo dyes, the triphenylmethane dyes, the phthaleïns, and the azines have been considerably modified, while those treating of the flavones and the sulphur dyes are entirely new.

The author has had the advantage of the very valuable assistance of Dr. C. Duisberg, Director of the Farbenfabriken, formerly Friedrich Bayer & Co., of Elberfeld, in reading the manuscript of both editions.

The book is an excellent one and can be heartily recommended to those desiring to study the chemistry of the dye-stuffs. The translator has, however, omitted several features of the original and thus made the translation decidedly inferior to it. For example, in the original only the most important facts are printed in large type, detailed information being given in smaller type. This was of great advantage to the beginner, as he could omit that part of the book printed in small type and yet have a complete survey of the subject. In the translation, everything is printed in the same type, whether it is important or unimportant, and in several instances information, which in the original was contained in foot-notes, has been put into the body of the book.

Again, the table of abbreviations, contained in the original, has been left out of the translation, but the abbreviations are used. This is a very important matter, for these abbreviations are used on nearly every page of the book. How is a student to know, without being told, that the letters B. or B. A. S. F. after the name of a dye-stuff mean that that dye is made by the Badische Anilin und Soda Fabrik.

The special literature of the dye-stuffs, given at the end of the book, has also been omitted from the translation, so that, if the reader is interested in a particular group of dyes and wishes to know where the original sources of the information contained in

the book are to be found, he would have to go to the German edition of the book.

The translation contains several inexcusable mistakes. For example, on page 3 the statement is made that aniline is a dye-stuff, and on pages 52 and 53 that nitroso-compounds are formed when *sulphurous acid* is allowed to act on phenols. The German terms benzol and toluol are used throughout the book in place of benzene and toluene. On pages 62 and 63, sodium *nitrate* is used for sodium *nitrite* in diazotizing salts of primary amines.

Those who read German at all readily, will find it advantageous to purchase the German edition of the book. For those who read only English, the translation is the best book on the subject now available, notwithstanding the many errors of translation.

W. R. ORNDORFF.

LES DÉRIVÉS TARTRIQUES DU VIN. PAR LE DR. P. CARLES. Troisiéme Edition. Bordeaux: Feret et Fils; Paris: Libraires Associés, Editeurs. 1903. 169 pp. Price, 4 fr. 50. Franco poste, 4 fr. 80.

The brochure before us, in its third edition, offers the results of years of study and practice in the recovery and utilization of the tartaric products obtained from wine and its residue, and its value has been recognized by the Institut de France in the award of the Montoyon prize of 2000 francs to the author. It is well worthy of the careful consideration of those interested in tartaric materials. In his valuable little work, Dr. Carles discusses the methods whereby these products are recovered and the different forms in which they are sent to the market. This is followed by thorough discussion of the analytical methods—described in detail—which are employed for the valuation of the various crude products. Generally these consist in (1) determination of the quantity of potassium bitartrate (the "actual test" of the United States), (2) the determination of the total tartaric acid present as potash and lime salts ("total test").

The first is comparatively simple and, according to Dr. Carles as well as in the experience of the reviewer, gives accurate results The second is complicated by the presence of various foreign substances in the crude tartars, and the method of Goldenberg, Geromont & Co., most widely employed, often gives results which,

according to Dr. Carles, are low in proportion to the quantity and character of the non-tartaric constituents in the material to be tested. To avoid these difficulties, Dr. Carles has devised a method in which the total tartaric acid is precipitated and weighed as tartrate of lime.

Discussing the choice of methods to be employed, Dr. Carles says: "Reviewing what has been said, we see that we must seperate and determine.

"1. Potassium bitartrate alone.

"2. Tartaric acid existing in mixtures of potassium bitartrate and calcium tartrate.

"3. Tartaric acid existing as tartrate of lime.

"For potassium bitartrate alone, in form of crude tartar, the same value is to be accorded to the methods of Teschemacher, Klein, and the 'Actual.'

"For lees, particularly low-grade, viscous and gummy, the American 'actual test' is the best.

"For mixed tartrates, with predominance of bitartrate, of value simply for the content of tartaric acid, the Goldenberg method of 1898 is to be recommended.

"When tartrate of lime is of importance or predominates in a crude tartar, the method of Carles, of 1903, is preferable.

"For factory residues, containing phosphates of iron, lime and alumina, plaster and tartaric acid, in unknown forms, there is little choice between the method of Goldenberg of 1898 and that of Carles of 1903."

The author, furthermore, discusses adulteration of crude tartars, a subject of interest and importance to refiners. In addition to this, attention is given to the many details of the tartar industry, offering information obtained by long experience and of value to all interested in the important industry under consideration

In his letter, transmitting his book, Dr. Carles says: "I shall be happy to send other copies of the book to those of your members who may wish it, or to those of your manufacturers, who may ask for it." It is practically the sole authoritative exposition of the subject, and it is, therefore, of great practical value.

WM. MCMURTRIE.

DESCRIPTIVE CHEMISTRY. By LYMAN C. NEWELL, PH.D., Instructor in Chemistry, State Normal School, Lowell, Mass. D. C. Heath & Co. 1903. 590 pp.

The success of the author's "Experimental Chemistry" caused the issuance of a readable "Descriptive Chemistry" from the same publishers. The book is divided into two parts: The first "contains the text, together with exercises and problems"; the second gives the experiments (179 in number). To the former is added an appendix with the metric system, valuable problems, enough of crystallography, some history and biography, table of atomic weights, and a wholesome list of reference books. To the second is added sane advice concerning equipment of the laboratory and generous, but economic, utilization of the necessary chemicals for the course given.

In passing opinion upon a book of this class, one is confronted with the extreme points of view advocated for an elementary course in chemistry; *viz.*, it should be for the accumulation of a large number of facts or for general culture purposes and training in scientific methods. It is a distinct success in the former and does not fail in the latter, altogether. Decidedly, the modern trend has been to follow the periodic system (whether it be true or not, is not the question), or quickly lead to it. In this book, the periodic classification of the elements is arrived at only after one has read 398 pages, just 38 pages before the close of the text proper.

The use of formulas is so gradually introduced that the student does not become frightened. Chapter IX, on Equivalents, Quantitative Significance of Equations, is particularly clear, while Chapter X, on Light, Heat, Electricity and Chemical Action, is clever and holds the attention.

Regarding the theory of electrolytic dissociation or ionization, one would prefer reading "most recently put forward" instead of "now generally held." Many of the modern practices are clearly explained in large type, often with illustrations, as, for example, the Castner process. Fine print suffices for the Leblanc and Solvay processes.

The arrangement which brings into consideration the carbon oxides, cyanogen, sulphocyanates and potassium ferrocyanide before methane, etc., or even before the student has been introduced

to sulphur, may be questionable, or only a matter of opinion. On page 18, the negative sign is omitted before the figures for the boiling-point of oxygen. All sapphires are by no means blue.

We like the remark under the photogravure of Joseph Priestley, "the discoverer of oxygen," better than that under Sir Humphry Davy, "the famous English chemist whose brilliant discoveries have never been surpassed."

The experiments in Part II are not only carefully selected, but are accompanied with searching questions. To be sure, in some cases (p. 485), the answers are given in the next paragraph.

The typography is all right and the index shows the care exercised in the making, for it is excellent. After all, *the* question to which a text-book should answer is, "Is it teachable"? The answer here is an emphatic affirmative. CHAS. BASKERVILLE.

SIMPLE METHOD FOR TESTING PAINTERS' MATERIALS. By A. C. WRIGHT, M.A., B.Sc. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 163 pp. 8 illustrations. First Edition, 1903. Price, $2.50 net.

The author states, in his preface, that the book is designed to enable the painter and paint-dealer to test and value the materials they buy, and the manufacturer and dealer the samples submitted to them, in the simplest manner, both in regard to practical properties and composition, the latter term used more in a manufacturing than in a purely chemical sense.

In a short introduction the author emphasizes the necessity of testing pigments and paints, and establishing and preserving reference standards. Some 30 pages are next devoted to a description of the apparatus and reagents to be used in the tests. The remaining 117 pages are devoted to a discussion of the mechanical and chemical properties and tests for impurities of dry and paste colors, liquid and gloss paints, varnishes, driers, linseed oil and turpentine.

A book of this kind must necessarily be incomplete and, to some extent, unsatisfactory. It is true that there are many tests for impurities and inferior or debased quality that can be made by the class to which this book is mainly addressed—dealers and practical paint-users—and confidence placed in the results. But, on the other hand, there are many varieties of paints and oils on the market whose quality can only be judged by the analyses of a

competent chemist, analyses that are too difficult and require too much apparatus to be attempted by the layman. The author recognizes this difficulty and very properly cautions against a charge of fraud on the part of the manufacturer or dealer, unless based on the analysis of a chemist.

The various tests given are, for the most part, qualitative, and in full detail, the varieties of paints most in use being treated at length. Besides the tests that are well known, several not in common use, are described. The book is well worth the price to the user of paints and contains much information on the subject that he will appreciate, and the general analyst also will find many points that will be of assistance in his analytical work. The proof-reading has been carefully done, though a few sentences read strangely—as where he speaks of the "efflorescence of carbonic acid" on warming lead carbonate with dilute nitric acid.

The printing and paper are up to the standard of the publishers, and the book has a good index. FRANK JULIAN.